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THE FEASIBILITY OF USING VANADIUM AND NICKEL TO TRACK OIL SPILLS IN COASTAL ENVIRONMENTS

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

The Department of Oceanography and Coastal Sciences

by
Sean Patrick Kenny
B.S., Louisiana State University, 2010
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TABLE OF CONTENTS

ACKNOWLEDGEMENTS ii

LIST OF TABLES vi

LIST OF FIGURES viii

ABSTRACT ix

CHAPTER 1. 1
1.1 Introduction and Literature Review 1
1.2 Crude Oil Production and Deposits 1
1.2.1 Land Sources 3
1.2.2 Sea Sources 3
1.3 Spills, Tracking, and Impacts 3
1.3.1 Land 4
1.3.2 Sea 4
1.3.3 Offshore Oil Spills and Their Impact On The Environment 5
1.3.3.1 Exxon Valdez 6
1.3.3.2 Gulf of Mexico Spills 6
1.3.3.3 Other Spill Events 7
1.3.4 Deep-Water Horizon Oil Spill in 2010 Gulf of Mexico 8
1.3.4.1 Amount Spilled 8
1.3.4.2 Impacts to Costal Areas 8
1.4 Current Oil Spill Plume Tracking Methods 9
1.4.1 Much Effort Put Into Tracking Spilled Oil 9
1.4.2 Difficulty of Tracking: Floating, and Subsurface Plumes May Travel Different Directions 11
1.5 Samples Processing and Analysis for Tracking Oil Spills 11
1.5.1 Collecting Water Samples 11
1.5.2 Processing Water Samples for GC and GC/MS Analysis and Instrument Setup 12
1.5.3 GC and GC/MS Analysis Most Reliable Analytical Tool 13
1.5.4 “Fingerprinting” of Oil for Identifying an Oil Source and Tracking Purposes 13
1.5.5 Sampling, Sample Processing, and Analysis of Water Samples Require Much Time and Expense 14
1.6 Need for Alternative Tracking Methods to Compliment Current Methods 15
1.6.1 Alternative Tracking Methods Should Be Easier, Quicker, and Less Expensive 17
1.6.2 Possibility of Using Trace Metals Associated with Crude Oil Deposits as a Complimentary Tracking Tool 17
1.6.3 Published Vanadium and Nickel Concentrations in Crude Oil . 18

1.6.4 A Range from Very Elevated Concentrations of Vanadium and Nickel in Some to the Reality of Low Levels in Other Crude Oil Sources 19
1.7 Methods of Measuring Vanadium and Other Trace Metals in Crude Oil-Impacted Water 22
1.7.1 Instrumental Methods 22
1.7.2 Water Sample Collection for Trace Metals 24
1.7.3 Sample Processing Required for Metals in Water Samples is Minimal 25
1.7.4 Analysis by ICP 26
1.7.4.1 Detections Limits 27
1.7.4.2 Useful Modifications of ICP Instrumentation 28
1.8 Possibility of Using Crude Oil Source Trace Metals such as Vanadium for for Tracking Plumes and Identifying Impacted Sea and Coastal Bay Sediments 33
1.8.1 Different Crude Oil Sources Contain Highly Variable Concentrations of Vanadium 34
1.8.2 Measuring Vanadium and Trace Metals in Sediments 34
1.8.2.1 Speciation of Vanadium in Crude Oil 35
1.9 Extraction Methods 36
1.10 Typical Background Vanadium Levels in Soils 36
1.11 Evaluation of Sediment Vanadium Levels 37
1.11.1 Total Concentrations not Sufficient for Evaluating Impacted Areas 37
1.11.2 Use of Trace Metal Ratios with Iron and Aluminum to Normalize Concentrations 38
1.11.3 Importance of Generating Background Data for Vanadium Concentrations and Vanadium/Iron and Vanadium/Aluminum Ratios in Uncontaminated Sediments 43
1.11.4 Why Vanadium and Nickel May Increase Residual Weathered Crude Oil 43
1.12 Study Objectives and Rationale 44

CHAPTER 2 46
2.1 Materials and Methods 46
2.2 Samples 47
2.3 Sample Processing 48
2.3.1 Sediments 48
2.3.2 Water 49
2.4 Analysis by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer 49
2.4.1 Detection Limits 49
2.4.2 Useful Modifications of Instrumentation 49
2.5 Statistics 49

CHAPTER 3 55
3.1 Results and Discussion 55
3.2 Element Relationships in Soils and Sediments 55
3.3.1 Vanadium and Nickel Versus Aluminum and Iron in Background Soils and Sediments 55
3.3.2 Vanadium Evaluation in Areas Known to Have Contaminated Sites 63
3.3.2.1 V/Al Comparison to Wax Lake as a Control 63
3.3.2.2 V/Al Comparison to Pre-spill GoM as a Control 66
3.3.2.3 V/Fe Comparison to Wax Lake as a Control 68
3.3.2.4 V/Fe Comparison to Pre-spill GoM as a Control 71
3.3.3 Nickel Evaluation in Areas Known to Have Contaminated Sites75
3.3.3.1 Ni/Al Comparison to Wax Lake as a Control 75
3.3.3.2 Ni/Al Comparison to Pre-spill GoM as a Control 77
3.3.3.3 Ni/Fe Comparison to Wax Lake as a Control 80
3.3.3.4 Ni/Fe Comparison to Pre-spill GoM as a Control 82
3.3.4 Zinc Evaluation in Areas Known to Have Contaminated Sites . .86
3.3.4.1 Zn/Al Comparison to Wax Lake as a Control 86
3.3.4.2 Zn/Al Comparison to Pre-spill GoM as a Control 89
3.3.4.3 Zn/Fe Comparison to Wax Lake as a Control 91
3.3.4.4 Zn/Fe Comparison to Pre-spill GoM as a Control 93
3.3.5 Magnesium Evaluation in Areas Known to Have Contaminated Sites 96
3.3.5.1 Mg/Al Comparison to Wax Lake as a Control 96
3.3.5.2 Mg/Al Comparison to Pre-spill GoM as a Control 98
3.3.5.3 Mg/Fe Comparison to Wax Lake as a Control 101
3.3.5.4 Mg/Fe Comparison to Pre-spill GoM as a Control . . . 103
3.4 Vanadium and Nickel versus Calcium and Magnesium in Water 106
3.5 Overall Implications for Sediment Data and Analysis 108
3.5.1 Likely Concentration of Vanadium and Nickel in Weathered Macondo Crude Oil 108
3.5.2 Analysis of V and Ni Concentration Ratios with Fe and Al 108
3.6 Conclusion 114

LITERATURE CITED 117

APPENDIX 125

THE VITA 128

LIST OF TABLES

Table 1.1. Levels of Selected Metals in Different Crude Oil Sources (modified from Table 8 from Appenteng et al., 2012) 18
Table 1.2. Different Concentrations of V, Ni, and V/Ni in Crude Oils 19-20
Table 1.3. Properties of Selected Heavy Fractions Post Refining 20
Table 1.4. Estimated Detection Limits, Alternate Wavelengths, and Suggested Wavelengths (Adapted from Eaton, 2005) 28
Table 1.5. Table Modified from "ICP-MS, or ICP-AES and AAS? –a comparasion" to Illustrate Improved Detection Limits with Axial Orientation (Tyler, 1994) 31
Table 3.1. V vs Al ANOVA for Sites in the Gulf of Mexico Region Using Wax Lake as a Control Site 65
Table 3.2. V vs Al ANOVA for Sites in the Gulf of Mexico Region Using Pre-spill GoM as a Control Site 68
Table 3.3. V vs Fe ANOVA for Sites in the Gulf of Mexico Region Using Wax Lake as a Control Site 70-71
Table 3.4. V vs Fe ANOVA for Sites in the Gulf of Mexico Region Using Pre-spill GoM as a Control Site 73
Table 3.5. Ni vs Al ANOVA for Sites in the Gulf of Mexico Region Using Wax Lake as a Control Site 77
Table 3.6. Ni vs Al ANOVA for Sites in Gulf of Mexico Using Pre-spill GoM as a Control Site 79-80
Table 3.7. Ni vs Fe ANOVA for Sites in the Gulf of Mexico Region Using Wax Lake as a Control Site 82
Table 3.8. Ni vs Fe ANOVA for Gulf of Mexico Samples Using Pre-spill GoM as a Control Site 84-85
Table 3.9. Zn vs Al ANOVA for Sites in the Gulf of Mexico Region Using Wax Lake as a Control Site 88
Table 3.10. Zn vs Al ANOVA for Sites in the Gulf of Mexico Region Using Pre-spill GoM as a Control Site 90
Table 3.11. Zn vs Fe ANOVA for Samples from Gulf of Mexico Using Wax Lake as a Control Site 92-93
Table 3.12. Zn vs Fe ANOVA for Sites in the Gulf of Mexico Using Pre-spill GoM as a Control Site 95
Table 3.13. Mg vs Al ANOVA for Gulf of Mexico Samples Using Wax Lake as a Control Site 98
Table 3.14. Mg vs Al ANOVA for Gulf of Mexico Samples Using Pre-spill GoM as a Control Site 100-101
Table 3.15. Mg vs Fe ANOVA for Gulf of Mexico Region Using Wax Lake as a Control Site 103
Table 3.16. Mg vs Fe ANOVA for Gulf of Mexico Samples Using Pre-spill GoM as a Control Site 105
Table 3.17. V, Ni, Mg, and Ca in Water Samples from Gulf of Mexico Using Brackish Louisiana Bays A and J as a Control Site 125-127

Table 3.18. Comparison of the Three Statistical Methods in Indicating Elevated Sediment V or Ni 112
Table 3.19. Summary of Mean and Median Z-Scores of Approximated Studentized Values 113

LIST OF FIGURES

Figure 1.1. Vanadium in Porphyrin Ring Structure 21
Figure 1.2. Trace Metal : Aluminum Ratios from Areas in South Louisiana 41
Figure 2.1. Approximated Studentized Values of Wax Lake 52
Figure 3.1. V and Ni Versus Al and Fe in Sediment Samples from Wax Lake 57-58
Figure 3.2. V and Ni versus Al and Fe in Sediment Samples from Pre-spill GoM .59-60
Figure 3.3. Wax Lake and Pre-spill GoM Comparison for V and Ni vs Al and Fe . 61-62
Figure 3.4. V vs Al for Sites in the Gulf of Mexico Region and Approximated Studentized Values Using Wax Lake as a Control Site 64-65
Figure 3.5. V vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site 67
Figure 3.6. V vs Fe for Sites in the Gulf of Mexico Region and Approximated Studentized Values Using Wax Lake as a Control Site 69-70
Figure 3.7. V vs Fe for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site 72-73
Figure 3.8. Ni vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Wax Lake as a Control Site 76-77
Figure 3.9. Ni vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site 78-79
Figure 3.10. Ni vs Fe for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Wax Lake as a Control Site 81
Figure 3.11. Ni vs Fe for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site 83-84
Figure 3.12. Zn vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Wax Lake as a Control Site 87-88
Figure 3.13. Zn vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site 89-90
Figure 3.14. Zn vs Fe for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Wax Lake as a Control Site 91-92
Figure 3.15. Zn vs Fe in Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site 94
Figure 3.16. Mg vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Wax Lake as a Control Site 97
Figure 3.17. Mg vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site 99-100
Figure 3.18. Mg vs Fe for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Wax Lake as a Control Site 102
Figure 3.19. Mg vs Fe for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site 104-105

ABSTRACT

Crude oil has been increasing in world demand over the past century. It is known that oil is resistant to weathering processes and if spilled, can cause serious environmental damage to an area, on land or sea. A complementary approach to current methods of tracking oil and identifying spill-impacted sediments may be to measure trace metals associated with crude oil. Trace metals, such a vanadium (V) and nickel (Ni) are known to be elevated in concentration in some oil sources, but little work has been done on this topic. This research explored less expensive and time-consuming methods to track or identify an oil spill-impacted area using the trace metals V and Ni that would serve as a complementary method to current GC/MS analyses. Using a ratio of extractable V and Ni versus conservative background elements found in abundance in sediments where this ratio may change as a result of oil spill contamination, it looks possible to determine if there is an elevated concentration of V and Ni in spill impacted areas compared to control areas. Two control sites, Wax Lake in the Atchafalaya Basin, and an area in the Gulf of Mexico near the Deepwater Horizon impact site, but sampled pre-spill, were compared to other sites, one known for most samples to have been impacted by the spill and other areas with more isolated contamination. Three different statistical techniques were used to compare possible impacted sites to control sites. The analyses covered ratios of V/Al, V/Fe, Ni/Al, and Ni/Fe to test for contamination, and Zn and Mg ratios to serve as control elements that should not be changed by a spill. Two of the three statistical methods generally supported the visibly oil impacted area had elevated concentrations of V and Ni. This work concludes that it

may be possible to use these V and Ni ratios to determine areas of crude oil contamination of sediments in coastal areas.

CHAPTER 1

1.1 Introduction and Literature Review

This research is focused on evaluating selected elements that are often found in crude oil as a possible supplementary means to track spilled petroleum in coastal systems and identify impacted areas. Crude oil's origins are ancient organisms that were buried millions of years ago. While crude oil is valuable for its many hydrocarbon compounds that can be refined and used as fuel and for other purposes, relatively small amounts of trace metals found in crude oil might be useful in supplementing established methods for tracking spills and spilled-impacted areas. This high-energy fuel has been in increasing demand over the past century as a major source of non-renewable natural energy (Yapa and Chen 2004; Walters et al., 2007).

1.2 Crude Oil Production and Deposits

Photosynthetic organisms that inhabited the earth millions of years ago formed crude oil. These photosynthetic organisms, such as certain types of algae, and other land plants have the ability to fix CO_2 into their own biomass and contribute a lot of organic matter in a given ecosystem. If the remains of these photosynthetic organisms are not utilized by other biota in the water column, then they are left to collect and be buried by sedimentation on the bottom of the ocean, where, in anaerobic sediments, they are not subject to rapid oxidation and mineralization back to CO_2 as predominantly occurs in oxidized environments (Gambrell et al., 1991). The remains of these organisms are then subject to microbial modification in the absence of oxygen. These organic layers will mix with

benthic sedimentary rocks over time and become buried under other benthic sedimentary rock layers, cap rock, thus burying the initial layer and creating source rock. Source rock refers to rock that is able to produce crude and cap rock refers to a non-permeable rock layer under which crude oil has been trapped (Walters et al., 2007). Petroleum source rock is a water-deposited sedimentary material that consolidates into rock, which contains an adequate amount of organic matter to be able to produce and release crude oil or natural gas when heated (Walters et al., 2007). As these sedimentary layers are packed on top of one another, a massive amount of pressure is produced, forcing the initial source rock further down into the earth's crust. It is in this long time frame of geological processes that immature sedimentary source rock begins to house the formation of a condensed organic carbon structure named kerogen. Kerogen formation and diagenesis initially occurs when dead cells are introduced to the biogeochemical activity of the earth. After this occurrence, microbial degradation processes break down the remaining organic macromolecules, further transforming the kerogen into more biologically resistant materials. Finally, several chemical reactions alter kerogen's remaining biochemical functional groups, such as carboxylic and amino acids (Walters et al., 2007). The final chemical process of catagenesis, a temperature, time, and pressure dependent process that involves the cracking of kerogen, forms a liquid substance that is rich in hydrocarbons from the source rock. This crude oil, being less dense than water, then undergoes an upward migratory process through mineral pores and permeable rock until it hits the petroleum trap rock (Walters et al., 2007).

1.2.1 Land Sources

The United States federal land and non-federal land production of oil is an estimated 4,287,000 barrels per day for the year of 2011 (US Energy Information Administration, Annual Energy Review, August 2011).

1.2.2 Sea Sources

The United States federal and non-federal production of crude oil from the oceans is an estimated 1,371,000 barrels per day for the year of 2011 (US Energy Information Administration, 2011). World total production is estimated at 74,043,000 barrels per day (US Energy Information Administration, 2011).

1.3 Spills, Tracking, and Impact Sites

The methods and tools used for the exploration and recovery of crude oil from deep reservoirs have significantly progressed over the years. Disturbances in the rock of a suspected reservoir area can lead to changes in pressure or the premature rupture of an oil reservoir. Premature rupture can lead to an oil blowout causing massive amounts of oil to seep from the rupture into the surrounding deep-water area (Nikravesh et al., 2003). Aside from anthropogenic interaction in a formation with crude oil, there are natural oil seeps, crude oil that was unable to be trapped after undergoing catagenesis, which expel oil over time where the volume released is suspected to be equivalent to a major oil spill on an annual basis (Nikravesh et al., 2003). These natural seeps are dispersed over a wide area thus more diluted and cause less of an impact at a local level compared to a more concentrated crude oil spill.

The exploration and recovery of crude oil to meet the demand of this natural fuel has resulted in many accidents resulting in spilling of crude oil in deep-water environments and on land systems alike (Bandara and Yapa, 2011).

1.3.1 Land

On land, the most frequent type of oil spill that occurs is due to a pipeline rupture. These ruptures are easily found due to the obvious visual impacts and other damages they cause as well as pressure and flow sensors located in transport infrastructure (Simons, 1999). Loss of large amounts of flammable crude oil from a rupture at a high pressure requires immediate attention and sometimes causes chaos and the need for evacuation of premises (Simons, 1999). The amount of rupture incidents for the year 2011 was reported to be 595 by the US Department of Transportation: Pipeline and Hazardous Materials Safety Administration (PHMSA) with a total of 139,024 barrels spilled during these incidents (US Department of Transportation: PHMSA, 2012). Spills on land can also lead to runoff into aquatic environments and cause significant damage to an aquatic community (USEPA, 1999b).

1.3.2 Sea

Transport of spilled oil in surface and subsurface plumes in water can be more difficult to track, and it is harder to identify impacted areas and areas that may potentially be impacted shortly after a spill. There are several natural processes that consistently occur in marine environments affecting spilled crude oil over short-term and long-term time frames. These natural physical processes include emulsification, evaporation, oxidation, microbial decomposition, and other

weathering processes. Furthermore, selective distribution of the different hydrocarbon compounds in crude oil in an ocean environment can increase the recovery effort in the environment affected by an oil spill, and also greatly increase the difficulty of tracking and determination of areas that have been impacted by the spill (USEPA, 1999b). These processes cause the oil to develop a non-uniform vertical plume in a deep-water column due to the spilled oil undergoing chemical and physical changes and particular fractions of crude oil compounds interacting with water at various depths differently. Emulsification occurs due to wave energy and motion causing two different types of emulsions that can greatly hinder dispersion of an oil slick. These emulsions give the illusion that oil has left the area and dispersed, however the emulsions can linger for years in an environment. Evaporation and oxidation of some lighter weight spilled oil components can cause larger molecular weight fractions of oil to sink in the water column by different modes of action. Evaporation causes volatile constituents of spilled oil to vaporize at the surface and leave behind the heavier constituents of oil that may float to the surface, get transported in the water column, or some oil components may sink to the bottom (USEPA, 1999b).

1.3.3 Offshore Oil Spills and Their Impact On The Environment

The accidental release of crude oil can lead to environmental damage and serious economic impacts. Understanding oil exploration, drilling, recovery, and oil spill tracking methods can ultimately yield useful knowledge limiting the oil's potentially damaging interactions with its surrounding ecosystem. The impacts of an oil spill can last for years as many crude oil compounds have resistance to

biodegradation by microbes. It is important to note that oil spill impacts have been documented for many years in multiple ecological studies (Bandara and Yapa, 2011).

1.3.3.1 Exxon-Valdez

The T/V *Exxon Valdez* was a tanker-grounding incident in Prince William Sound of Alaska that occurred March 24th, 1989. The wreckage released 258,000 barrels of crude oil (Rice et al., 2001). The oil contaminated substantial amounts of the land-sea environment affecting several indigenous organisms. Many animals were studied to gauge the effects of this oil being introduced into a previously uncontaminated system. The long-term effects of this oil spill are well documented and are still ongoing (Rice et al., 2001).

The pink salmon fishery in Prince William Sound has been investigated thoroughly after this incident. In a report published in 2001, there were several notations of pink salmon having, "elevated embryo mortality in oiled streams…" and "environmental damage through several mechanisms, including the toxicity associated with ingestion or adsorption through the biota's respiratory structures or skin; coating or smothering" (Rice et al., 2001). Furthermore, the report offered evidence that even weathered oil is persistent and biologically available for long periods of time.

1.3.3.2 Gulf of Mexico Spills

Ixtoc I was an oil spill that occurred in the Bay of Campeche of the Gulf of Mexico on June 3rd, 1979. This oil spill was estimated to have spilled anywhere from 10,000 to 30,000 barrels of oil per day until the wellhead was capped on March 23,

1980 (Boehm and Flest, 1982). Significant amounts of chemical dispersants were used along with containment booms to minimize damage. The oil slick however, still spread north of the well and then west despite on-site response actions, affecting several coastal beach areas and estuaries (Boehm and Flest, 1982). The Ixtoc I spill had detrimental effects on parts of the Texas coastal environment and on a rare nesting area for the Kemp's Ridley sea turtle, which caused a decrease in the survival and developmental deformities of offspring (Milton et al., 2003, Hall et al., 1983).

1.3.3.3 Other Spill Events

On August 10, 1993, in Tampa Bay, Florida, three marine vessels collided near the entrance to the Bay area. In this collision, the barge *Bouchard B-155* spilled an estimated 7,809 barrels of oil into the surrounding Bay area. The coastal areas impacted, Madeira Beach, Treasure Island, and St. Petersburg Beach, all received heavy oiling. These areas are popular for recreation and include nesting areas of indigenous turtle species. The coastal profiles of the beaches were changed due to spill clean up and seasonal storm erosion (Davis et al., 1995). Environmental effects of oiling in the island keys area were observed and were particularly harsh for the mangrove species in this area. These mangroves, which provide shelter for bird species and several other marine animals, were exposed to medium to heavy oiling and experienced anywhere from 35-50% mortality for select areas (Levings and Garrity, 1995).

1.3.4 Deep-Water Horizon Oil Spill in 2010 in Gulf of Mexico

1.3.4.1 Amount Spilled

The United States Government estimated 4.9 million barrels of Macondo sweet crude oil were released from the failed wellhead structure over 87 days (Zengel and Michel, 2011).

1.3.4.2 Impacts to Coastal Areas

A total of 1046 kilometers of the Gulf of Mexico and coastal bay shorelines were oiled from the Deepwater Horizon oil spill exposing 40% of the nation's most productive wetland ecosystems to potentially devastating environmental trauma (Zengel and Michel, 2011). Damages from the Deepwater Horizon spill oiling these shorelines impacted marshes that are invaluable to the Mississippi River delta ecosystem. The Louisiana wetland habitats are a vital contributor for supporting and protecting fisheries (30% of the national fish production) and protecting the oil and gas industries' infrastructure, which provide one-third of the nations oil and gas production, from crippling storms (Mendelssohn et al., 2012). Deterioration of the wetlands promotes loss of basic anthropologic economic base due to loss of soil and ground available for petroleum infrastructure and cultural development. Recreational use such as waterfowl hunting, bird watching, and fishing are adversely impacted due to wetland loss. Most importantly, loss of the wetlands will result in a decline of Louisiana's coastline, coastal wetlands, and the ecological value of these wetlands (Farber, 1996). About 725 kilometers of Louisiana's shoreline were oiled, where the most affected region of Louisiana was in the Bay Jimmy area of Barataria Bay (Zengel and Michel, 2011). Shorelines of the Bay Jimmy area were

heavily oiled with little to no vegetation survival (Zengel and Michel, 2011). There were variable impacts upon this region as oil density was variable from high oiling to moderate oiling. In the fall of 2011, it was reported that heavily oiled shorelines had little to no vegetation (Mendelssohn et al., 2012).

The wetlands of Louisiana continue to face the lingering effects from this oil spill as recent reports have stated, "Louisiana's Barataria Bay oiled marshes eroded at about twice the rate of non-oiled marshes" (Vastag, 2012). Brian Silliman also remarked on the after effects of the oil spill, "We already knew that erosion leads to permanent marsh loss, and now we know that oil can exacerbate it" (Vastag, 2012). Marshlands lost during the oil spill are unable to recuperate and will not "come back" (Vastag, 2012). The residual oil and effects of oil will persist in this area as it has been reported in recent news that Hurricane Isaac, in the fall of 2012, washed up tar balls along the beaches of Elmer's Island and Grand Isle (Reeves, 2012). It is uncertain how long the residual oil will remain in the Louisiana area and what long-term effects will occur, but it is certain that the oil spilled from the Deep-Water Horizon incident will remain a factor in loss of wetlands for some time in the future.

1.4 Current Oil Spill Plume Tracking Methods

1.4.1 Much Effort Put Into Tracking Spilled Oil

Response methods for tracking oil must first be evaluated by geographic location and water column considerations. The movement of the oil, thickness, and location of the crude oil in the given area must be known before undertaking a response method (Department of Environmental Conservation, 2006). There are two known tactics used in tracking oil spilled on land and water. "Plume

Delineation" is a term used to describe methods and equipment used to determine size, shape, and vector of oil spilled on land, while "Discharge Tracking on Water" depicts the methods and equipment used to track movement of oil on the water's surface and in subsurface plumes (Department of Environmental Conservation, 2006).

Tracking an oil slick on the surface of water requires a trained observer with the ability to detect an oil slick from an aircraft or aboard a marine vessel. That is the only direct method with the ability to accurately describe an oil slick's physical features, such as location, shape, size, weathered state, etc. (Department of Environmental Conservation, 2006). Both an aircraft and a marine vessel team are suggested in observing an oil slick, as an aircraft can better view and determine the area of the oil slick, and the marine vessel can physically sample the oil to assess its physical characteristics at the present time (Department of Environmental Conservation, 2006). These methods can only be utilized if the oil slick is visible.

Deep water oil spills require a more sophisticated approach of tracking as much of the impacted water is usually not visible from the surface. Methods utilized in tracking oil plumes at these depths are generally reliant on submersibles and cable-lowered sample collection devices (Camilli et al., 2010). These probes can be equipped with specialized instruments to sample, sense, or analyze petroleum hydrocarbons, such as the "*TETHYS* in situ membrane inlet mass spectrometer" (Camilli et al., 2010).

1.4.2 Difficulty of Tracking: Floating, and Subsurface Plumes May Travel Different Directions

If an oil slick is not visible due to natural obstructions such as fog, darkness, or inability to acquire observational air or watercrafts, then more indirect methods must be used in tracking the oil slick. Tracking buoys are sometimes a viable method if the oil slick cannot be viewed. However, much of the buoy tracking method is irrelevant if the buoy does not remain in the oil slick, and a surface buoy may not accurately reflect subsurface plumes. Tracking buoys can pinpoint oil slicks, as they contain a GPS tracking system, but cannot give information on the coverage or weathered state of the oil slick. These methods may include use of infrared cameras that require specific training to interpret the information and understand the present state of the oil, but become less effective as the oil slick interacts longer in the water column and equilibrates with ambient water temperature (Department of Environmental Conservation, 2006).

Subsurface oil plumes are difficult to track due to interplay of multiple mechanisms, such as gas and oil interactions with multiphase flow, gas hydrate formation, and solubility of oil constituents. These mechanisms cause the modeling of a deep-water oil plume to be difficult and the respective oil plume's dynamic interactions in the water column problematic to predict (Camilli et al., 2010).

1.5 Sample Processing and Analysis for Tracking Oil Spills

1.5.1 Collecting Water Samples

Crude oil spilled into the ocean is generally collected as samples in vials, jars, or on sorbent pads. Collecting of open water samples generally requires the use of a boat and it is advised to take samples from the bow of the boat to avoid

contamination of the sample from the vessel itself (International Tanker Owners Pollution Federation, 2012). Crude oil released from a deep seep or well can be monitored by field in situ measurements or collection of samples to be shipped to a laboratory. In situ field measurements require sensors that are specific for identifying and quantifying crude oil concentrations, for example a multi-wavelength fluorometer (International Tanker Owners Pollution Federation, 2012). Collection of samples at depth is possible when using specialized sampling vessels that descend closed and then when the desired depth is reach are switched open then re-sealed to isolate and retrieve the sample. Recovery of the device is specific to the type of device used (International Tanker Owners Pollution Federation, 2012). These samples can then be analyzed for the presence of oil by on-board instruments, or returned to a laboratory for analyses (Camilli et al., 2010).

1.5.2 Processing Water Samples for GC and GC/MS Analysis and Instrument Setup

This process can be done for seven or eight samples as a set by one technician. The extraction process is about three hours long (Dr. Overton, Edward. personal communication. November 7, 2012). As with all quality assurance procedures in a laboratory, there is a laboratory control blank, calibration standard, and quality control samples that are run with each batch of samples to ensure appropriate recovery and little to no contamination or interferences with the procedure (USEPA, 2010).

A sample cleanup process is advised after oil is extracted from the aqueous solution, but can be bypassed if the recovered oil/solvent matrix proves to be clean. Following cleanup of the extractant, the samples are now available for GC/MS

analysis. Tuning, followed by an initial calibration run, and then a sample set run for the GC/MS requires a lot of time as each sample can take about an hour to analyze. The initial calibration should be good for 12 hours of sample analyses for compounds of interest before recalibration is required (USEPA, 2007b).

1.5.3 GC and GC/MS Analyses Most Reliable Analytical Tool

As presented above, processing and analysis by GC/MS requires much technician time plus substantial expense associated with supplies and instrument maintenance. However, GC/MS is a reliable analytical tool with a high level of confidence in the results for specific petroleum compounds in crude oil (Kumar, 2009). Gas chromatography is a relevant technique in analyzing contaminated environmental areas of concern. Gas Chromatography (GC) with a flame ionization detector, and in particular, gas chromatography with a mass spectrometer detector (GC-MS), are instruments used to measure petroleum hydrocarbons associated with oil spills.

1.5.4 "Fingerprinting" of Oil for Identifying an Oil Source and Tracking Purposes

The source of particular spilled oil sampled in the environment can usually be identified. The procedure to identify the source of an oil is to compare the presence and concentration of specific petroleum hydrocarbon compounds in a sample and the ratio of selected compounds in the sample to compounds and concentration ratios of known sources until a positive identification beyond a reasonable doubt is found, or until the spilled oil is demonstrated to be from different sources (Gloves and Bullin, 1989). Crude oil is a mixture of many hundreds of individual petroleum hydrocarbon compounds at various

concentrations in the mixture (Gloves and Bullin, 1989). Identifying the ratios of selected key compounds in the mixture by GC/MS can be used to "fingerprint" an oil and determine if oil found some distance from a spill site is indeed from that spill site or possibly another source (Gloves and Bullin, 1989).

1.5.5 Sampling, Sample Processing, and Analysis of Water Samples Require Much Time and Expense.

Multiple considerations must be evaluated before conducting sampling, sample processing, and analysis of water samples for hydrocarbons (USCG: Marine Safety Laboratory, 2010). Oil spilled is subject to weathering and should be collected as soon as possible because continued weathering of the oil might further skew fingerprinting results. Alongside the contaminated water sample, a clean water sample should be taken for any area the contaminated water is sampled. This provides a "background" sample for comparison during later analyses (USCG: Marine Safety Laboratory, 2010). When interacting with the contaminated water sample it is pertinent that personnel use personal safety equipment. During the sampling process it is important to consider the surroundings in which the sample is collected. Certain hazardous chemicals, sewage, or other anthropogenic compounds may alter or interfere with the oil fingerprint. Notation is advised on all accounts if spilled oil has been sampled near or around an area where the fingerprint can be altered (USCG: Marine Safety Laboratory, 2010).

Application of chemical dispersants at an oil spill source can also interfere with fingerprinting. Mixing of chemical dispersants into crude oil over time, water depth, selective dissolution of particular hydrocarbon compounds as they move through the water column, and mixing points may serve to complicate instrumental

methods of tracking the crude oil's primary hydrocarbon components within the oil plume (Camilli et al 2010).

Sampling requires specific type of devices that have little to no interaction with the sampled oil to prevent contamination of sampled oil rendering the sample useless for a fingerprint analysis. Often gloves or any sorbent material will directly contaminate the oil sample. Oil samples should not come in contact with plastic and should only be kept in glass vials with metal or Teflon-lined caps. Even after samples are collected, they are still subject to weathering processes and should be analyzed as soon as possible for optimal results (USCG: Marine Safety Laboratory, 2010).

In summary, sample processing and analysis for GC/MS analysis for hydrocarbons in oil spill samples consumes a lot of resources, money, and time to produce results and is only able to process and analyze a maximum of approximately eight samples per day.

1.6 Need for Alternative Tracking Methods to Compliment Current Methods

Alternative plume tracking methods would not replace current methods with a proven track record, but might offer supplemental tracking data that can be made available more quickly and at less expense. There are two proven methods for studying an oil spill: specific and non-specific. Non-specific methods offer more rapid analysis, require a low sample preparation time, and are relatively inexpensive. The main drawback behind using non-specific methods is that the data produced do not have individual compound information or specific information linking the sample of spilled oil to the petroleum parent source (Fingas and Wang,

1999). Specific methods used in studying spilled oil are targeting for specific compounds that directly "fingerprints" an oil sample to its parent oil source. These tests typically involve a combination of gas chromatography with mass spectrometry, high-performance liquid chromatography, infrared spectroscopy, thin layer chromatography, supercritical fluid chromatography, fluorescence spectroscopy, or ultraviolet spectroscopy. These tests are used in complementing GC/MS when speed is of the essence in collecting and analyzing spilled oil samples (Fingas and Wang, 1999). These supporting techniques do not compete with the current specificity tests, such as GC/MS etc., but can collect data that complements GC/MS data (Fingas and Wang, 1999).

Polynuclear aromatic hydrocarbon (PAH) distribution pattern recognition is a supplementary method that takes advantage of PAHs' resistance to weathering and distribution in both crude and refined oil. These attributes make PAH fingerprint analysis a valuable technique for oil identification purposes (Fingas and Wang, 1999). Another powerful oil fingerprinting technique called petro-porphyrin analysis, uses metalloporphyrins to track a parent source for spilled oil. Petro-porphyrins are a product of microorganisms that have utilized metals, found in their surrounding environment, in their metabolism of chlorophyll. Vanadium and nickel are the target metals that are usually absorbed from microbes in the area and are often found in elevated concentrations in petro-porphyrins associated with crude oil (Fingas and Wang, 1999).

1.6.1 Alternative Tracking Methods Should Be Easier, Quicker, and Less Expensive

Using alternative supplemental methods stated above could become more cost effective than GC/MS. For example, PAH distribution pattern recognition can be used as a pre-test for GC/MS analysis to determine if sets of samples are of interest. Alternatives to GC/MS techniques are thus able to analyze larger numbers of samples and report in less time and at a substantially lesser cost than required for chromatography tracking of oil plumes.

1.6.2 Possibility of Using Trace Metals Associated with Crude Oil Deposits as a Complimentary Tracking Tool

Many crude oils contain one or more metallic elements that might be used as a tracer for observing the movement of oil in a water column as it is expelled from the site of a spill. Vanadium is an element that is often found to be higher in concentration in crude oil and in oil-impacted environments when compared to uncontaminated soils, sediment-water systems and seawater, and nickel is also another element that is often found to be elevated in crude oil (Andrade et al., 2004; Sasaki et al., 1998). Vanadium (V) and nickel (Ni) are elements that are observed in specific porphyrin ring structures that are found within crude oil (Duyck et al., 2007). Some crude oils are substantially elevated in V and Ni concentrations that may be useful in identifying or tracking a spill or evaluating spill-impacted sediments (Eslami et al., 1999).

1.6.3 Published Vanadium and Nickel Concentrations in Crude Oil

Crude oils across the world have a high variance of asphaltenes, the class of crude oil components in which the elements V and Ni are dominantly found. Due to this variance, the concentrations of V and Ni vary greatly among the different crude oil sources (See Table 1.1 adapted from Appenteng et al., 2012).

Table 1.1: Levels of Selected Metals in Different Crude Oil Sources (modified from Table 8 from Appenteng et al., 2012)

Country	Crude Oil/Field	Trace Element Levels (ug/g)				
		Co	Cu	Na	V	Ni
Ghana	Saltpond	2.86	0.293	101	3.71	12.6
	Jubilee	0.191	0.527	324	2.41	3.22
Nigeria	Opuama	0.017	1.86	13.6	0.11	0.82
	Egwa	0.613	5.01	89,137	0.85	5.03
	Sapele	0.008	2.58	<200	<0.2	0.54
	Benisede	0.99	6.25	249	0.19	2.7
	Forcardos	0.47	9.53	12,862	<0.34	1.89
	Afiesere	0.66	18.9	223	1.06	5.71
	Jones creek	0.28	9.46	304	0.64	4.33
	Utorogu	0.17	8.42	111	0.45	2.5
	Oben	0.01	2.88	23.2	0.05	0.72
	Uzere	0.36	10.7	352	1.2	4.64
China	Janghan	0.63		79.4	1.23	27.6
	Zhongyuan	2.55		17.2	3.68	36.5
	Shengli	8.87		113	1.28	62.9
	Liaohe	1.52		29.1	1.5	107
	Kalamayi	0.65	7.18	891	10.4	63.6
	Miyang	0.81		148	0.57	25.6
	Dongfeng				16.6	58.9
	Renqiou	0.14	5.89	25.3	0.66	19.7
	Dagang	0.46		91.8	0.09	10
	Songhuajiang	0.78	0.57	25.9	0.06	6.31
Canada		0.029		0.062	3.73	5.01
Venezuela		0.048		1.93	72	19

The significance of these data from Appenteng et al., (2012), is that V and Ni concentrations, as well as other crude elemental constituents, are variable in oils from around the world.

1.6.4 A Range from Very Elevated Concentrations of Vanadium and Nickel in Some to the Reality of Low Levels in Other Crude Oil Sources.

Modified Table 8 from Appenteng et al., (2012) is presented as Table 1.2, displaying differences in concentration of V, Ni, and V/Ni ratios from crude oils from fields in different nations.

Table 1.2: Different Concentrations of V, Ni, and V/Ni in Crude Oils

Country/Oil Field	Concentration in ug/g	Concentration in ug/g	Concentration in ug/g
	V	Ni	V/Ni
Ghana			
Saltpond	3.71	12.6	0.3
Jubilee	2.41	3.22	0.75
Nigeria			
Opauama	0.107	0.822	0.13
Egwa	0.853	5.03	0.17
Sapele	<0.108	0.54	<0.167
Benesede	0.193	2.7	0.071
Forcados	<0.176	1.89	<0.093
Afiesere	1.06	5.71	0.186
Jones Creek	0.637	4.33	0.147
Utorogu	0.453	2.5	0.181
Oben	0.054	0.724	0.075
Uzere	1.195	4.64	0.258
China			
Jianghan	1.23	27.6	0.045
Zhongyuan	3.68	36.5	0.101
Shengli	1.28	62.9	0.02

(Table 1.2 continued)

Country/Oil Field	Concentration in ug/g	Concentration in ug/g	Concentration in ug/g
Liaohe	1.5	107	0.014
Kalamayi	10.4	63.6	0.164
Miyang	0.57	25.6	0.022
Dongfeng	16.6	58.9	0.282
Renqiou	0.66	19.7	0.034
Dagang	0.09	10	0.009
Songhuajiang	0.06	6.31	0.01
United States			
California	82.4	193.8	0.425
Wyoming	298.5	112.9	2.65
South Louisiana	0.1	0.9	0.27

Below is Table 5-4 taken and modified from Speight, 2000, presented here as Table 1.3, that shows selected properties of select heavy fractions of oil after oil has been refined.

Table 1.3: Properties of Selected Heavy Fractions Post Refining

Crude oil Origin	Kuwait	Kuwait	Venezuela (east)	Boscan (Maracaibo, Venezuela)	Cabimas (Venezuela)
Residuum type	Atmospheric distillation	Vacuum distillation	Atmospheric distillation		Vacuum distillation
Nickel (mg/kg)	14	32	94	133	76
Vanadium (mg/kg)	50	102	218	1264	614

There is a substantial difference in concentrations of V and Ni in crude oils taken from petroleum around the world. While the tables given above show moderate to low levels of V in crude oils, V has been found in concentrations of up to 1,500 mg/kg in select heavy, or high density, crude oils (ATSDR, 2009). The reason for V having these large differences in concentration in heavy oil versus light crude oil stems from the unique vanadyl porphyrin ring structure within heavy crude oils (ATSDR, 2009).

V and Ni are found in porphyrin ring complexes that share a common structure to hemoglobin and chlorophyll (Treibs et al., 1936). Porphyrin rings consist of four pyrrole functional groups linked by methine (-C=) bridges and centralized imine functions (-NH-) that allow metals to bind via chelation (Speight, 2007). Porphyrin rings are naturally occurring molecules in petroleum and are known to be strong organic chelators that can bind metals, such as V or Ni (Speight, 2007).

Figure 1.1illustrates the porphyrin ring structure with vanadium as the centric ion.

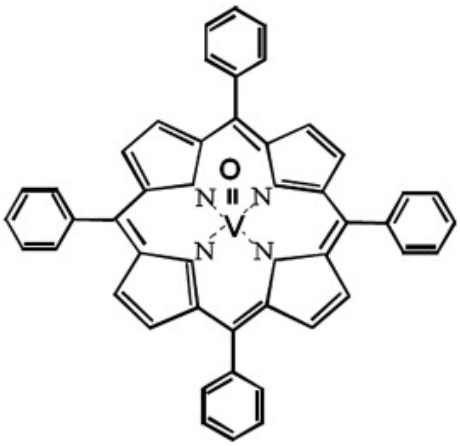


Figure 1.1 Vanadium in Porphyrin Ring Structure (Carciumaru et al., 2012)

However, not all V and Ni concentrations in crude oil are considered to be in the porphyrin ring form. V/Ni ratios were observed to be constant in crude oils of a common rock source, however this observation was dependent on the geological age of the rocks (Ball et al., 1960). Ni(II) and VO(II) are dominant in both porphyrin structure and in non-porphyrin complexes in crude oils and can be used as biomarkers which indicate the stratigraphic origin of petroleum in an area (Treibs et al., 1936); (Duyck et al., 2007).

1.7 Methods of Measuring Vanadium and Other Trace Metals in Crude Oil-Impacted Water

1.7.1 Instrumental Methods

There are several methods to measure trace metals. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) is an instrumental method that analyzes multiple elements at once using element-specific emission spectra to differentiate one element from the next, such as nickel from aluminum. This technique provides elemental concentration based on emission intensity at element-specific wavelengths where intensity of elemental emission spectra at one or more wavelengths is proportional to concentration. The ICP-OES is capable of analyzing many metals and nonmetals in an appropriate solution, including V and more than 65 other elements at detection limits between less than one to 50 micrograms per liter (Harris, 2010); (USEPA, 1994). Furthermore, ICP-OES has been successful in analyses for biological, environmental, and industrial samples for the trace element vanadium (Coetzee and Hu, 2007). Major advantages to this technique are relatively good sensitivity, the analysis of multiple elements simultaneously, speed of analyses, and often the minimal sample preparation required.

Processing water samples by chelation preconcentration coupled with Graphite Furnace Atomic Adsorption (GFAA), Flame Atomic Adsorption (FAA), or ICP analysis are techniques used sometimes to determine very low concentrations of trace elements in water samples. An "iminodiacetate functionalized chelating resin" is used to perform the preconcentration of specific trace metals. The preconcentration process is unique in that it directly isolates and concentrates the targeted trace metal ions into a matrix of nitric acid, manually removing most of possible interfering substances such as common salt ions in seawater. The preconcentration process is highly specific for a select few trace elements, such as cadmium (Cd), cobalt (Co), copper (Cu), lead (Pb), and nickel (Ni). The preconcentration then allows for ease of analysis with improved detection limits by the GFAA or other instrumental methods (USEPA, 1992). However, in crude oil impacted waters where metals such as V and Ni are already strongly bound by natural porphyrin ring chelation, the recovery of target metals may be low. This may be the case for most chelating agents used for naturally chelated metals in seawater. The following paragraph indicates a chelating approach that will recover V and Ni directly from crude oil, but the question remains for using synthetic chelating agents to recover porphyrin ring-bound V in crude oil dispersed in seawater.

Reverse-phase High-Performance Liquid Chromatography (HPLC) is a specific method used in measuring trace metals in crude oil. This method uses a strong chelating agent, 4-(2-pyridylazo)resorcinol (PAR) to separate and determine select trace metals, such as chromium (Cr), vanadium (V), nickel (Ni), and copper

(Cu) (Eslami et al., 1999). The PAR chelate binds to the select trace metals found in crude oil, and then after chelation the select trace metal-PAR complex, e.g. V-PAR, is ready for analysis. The reverse-phase HPLC is used to produce chromatographic separation and determination of selected metal chelates (Eslami et al., 1999). The retention time in the column determines the recovery and identity of the bound element, as certain PAR bound elements separate and remain in the column at various times before they reach the spectrophotometric detector (Eslami et al., 1999). This technique requires little effort and is successful at speciation of multiple trace-metal chelates at once (Eslami et al., 1999). In summary, the technique uses the PAR chelating agent to recover free and porphyrin ring bound trace metals.

1.7.2 Water Sample Collection for Trace Metals.

The sample collection procedure for water possibly contaminated with oil for analyses of trace metals is similar to the previous sample collection procedure described earlier in this chapter for samples intended for processing for hydrocarbon analyses. The major difference in trace metal sample collection is the relative ease of preserving and processing the sample for metals analyses. The sampling procedure requires two people with specific assigned tasks and for those people to remain in their roles as deviation from the sampling protocol may introduce contamination to samples collected (USEPA, 1996). Clean shoulder-length polyethylene gloves, PVC gloves, a polyethylene bottle, glove bag, and a closed storage container are the simple sample collection tools required (USEPA, 1996). One person, this person is noted as “clean hands” (USEPA, 1996), is to

handle the entire sampling process with extreme caution and documentation of sampling technique, area, and necessary physical observations. The other person, noted as "dirty hands" (USEPA, 1996), is to open, close, and seal any area or container that is not marked as being clean to avoid contamination of sample collected. If sample preservation is required, then a simple addition of "5 mL of 10% solution of ultrapure nitric acid in reagent water per liter of sample" can be used to preserve a pH-neutral sample to a pH of less than 2 until analyses (USEPA, 1996).

1.7.3 Sample Processing Required for Metals in Water Samples is Minimal

Unlike water samples being processed for organic analyses, sample processing for metals is simple and fast. However, some water samples in this research were processed due to algae being found in them. These algae cannot be overlooked as they may have absorbed trace metals that settle out with algae cells or are bound to algae cells stuck to container walls and must be digested to release metals from the algae cells so that the metals will remain in solution for analysis. However, even with the sometimes-added step of acid-digesting samples for algae cells, processing samples for metals analyses is much simpler and quicker than processing for organic analyses.

The digestion of a water sample by nitric acid can be used for samples with both high and low concentration analytes (Eaton, 2005). Specifically concerning low concentration or trace-level analytes, the procedure for sample processing requires a block heater step and a centrifuge step. Pyrex glass tubes should be acid-washed and rinsed with deionized water before pipetting of sample into the tube. This is to ensure little to no contamination occurs during the transfer. The initial

sample is digested in trace metal-grade nitric acid in the digestion tube on a block heater at 105 Celsius for at least two hours under a hood. It is important that the tubes should be capped to a point where vapors can still evacuate from the tube, but prevent contamination to the sample. Keep adding concentrated nitric acid until digestion is complete, or, you can also insert glass funnels in the top of the digestion tubes to facilitate refluxing of the acid to minimize acid loss as described by Hou et al., 2006. After digestion, the tubes are removed from the heater block and allowed to cool (Eaton, 2005).

1.7.4 Analysis by ICP

Analysis by ICP is fast and relatively inexpensive. The Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and ICP-Mass Spectrometry (ICP-MS) are instruments that have been used in measuring multielement analysis with excellent results. These instruments have been the industry staple for rapid analysis for simultaneous analyses of multiple elements in an aqueous solution with good detection limits (Donard et al., 2007). The processing of samples required for metals in water samples at a trace-level is minimal. On the instrument, 10 to 20 samples can be analyzed for all elements of interest per hour. Evaluating data output is simple as the data is reported in concentration and corrected with a reagent control blank if necessary.

The sample batch processing and extraction methods for preparation for organic compounds for GC/MS analysis can take up to 3 hours, is highly labor intensive, and may require pre-tests to determine if extractable suspended solids are present in the sample solution (Dr. Overton, Edward. personal communication.

November 7, 2012). In a day, the maximum number of organic samples that can be analyzed by GC/MS is eight (Dr. Overton, Edward. personal communication. November 7, 2012) compared to ICP analysis of 10-20 samples per hour (approximately 80 – 160 samples per day). Data analysis of organics in GC/MS requires a sample "cleanup" column, (a column that reduces build up of contaminates in the injection port area and improves peak resolution) for biological or environmental samples. This cleaning is done in form of cleaning columns. These cleaning columns cost around 20-30 USD if they are prepared and loaded in the lab, otherwise the columns can be purchased at the upwards of around 100 USD (Dr. Overton, Edward. personal communication. November 7, 2012).

1.7.4.1 Detection Limits

Detection limits for optical emission ICP instruments are good for a many elements, in the range of < 1 ppb (ug/L) to several ppb for many metals (Eaton, 2005).

Table 3120:I from Eaton, 2005 has been modified and presented below as Table 1.4 illustrating estimated detection levels and suggested wavelengths for ICP-OES analysis. The wavelengths shown are recommended for conventional pneumatic nebulization. Actual detection limits are sample-dependent and require observation to determine which wavelength is best for a specific sample. However, these detection limits reported by Eaton have been much improved by recent modifications to ICP such as described in the section to follow.

Table 1.4: Estimated Detection Limits, Alternate Wavelengths, and Suggested Wavelengths (Adapted from Eaton, 2005)

Element	Estimated detection Level (ug/L)	Suggested Wavelength (nm)	Alternate Wavelength (nm)
Aluminum	40	308.22	237.32
Antimony	30	206.83	217.58
Arsenic	50	193.7	189.04#
Barium	2	455.4	493.41
Beryllium	0.3	313.04	234.86
Boron	5	249.77	249.68
Cadmium	4	226.5	214.44
Calcium	10	317.93	315.89
Chromium	7	267.72	206.15
Cobalt	7	228.62	230.79
Copper	6	324.75	219.96
Iron	7	259.94	238.2
Lead	40	220.35	217
Lithium	4S	670.78	-
Magnesium	30	279.08	279.55
Manganese	2	257.61	294.92
Molybdenum	8	202.03	203.84
Nickel	15	231.6	221.65
Potassium	100S	766.49	769.9
Selenium	75	196.03	203.99
Silica	20	212.41	251.61
Silver	7	328.07	338.29
Sodium	30S	589	589.59
Strontium	0.5	407.77	421.55
Thallium	40	190.86#	377.57
Vanadium	8	292.4	-
Zinc	2	213.86	206.2

S = Sensitive to operating conditions

= Available with vacuum or inert gas purged optical path

1.7.4.2 Useful Modifications of ICP Instrumentation

Various supplemental devices can optimize an ICP for improved detection limits on different types of samples. The ICP plasma is a critical part of the instrument as it converts elements in the aerosol sample mist from the nebulizer to

a form that emits characteristic wavelengths of light where emission intensity is proportional to concentration. First a sample is introduced to the instrument with elements dissolved in a liquid. Second, the liquid sample is converted into a mist in the nebulizer chamber. This mist travels to the torch where the mist-containing elements of interest is exposed to the high temperature of the plasma in the torch. The plasma's temperature can range from 6,000 to 10,000 degrees Kelvin. At these temperatures, neutral (zero charge), free atoms of the elements in the sample are produced in an excited state and emit electromagnetic radiation (EMR). The EMR produced is specific wavelengths for each element where concentration is proportional to elemental emission intensity (Mermet, 2005).

The spatial orientation of the torch has been considered a useful option for improving detection limits of elements in some samples and is sometimes a point of contention as to what is best (Tyler and Goldstone, 2003). The ICP torch can be oriented in one of two ways in relation to the optical path of the instrument. These are the radial and axial orientations. The radial orientation of the torch is a vertical (upright) position and the optical path or entrance slit viewing point is perpendicular to the flow of plasma and its entrained sample mist. This orientation has a more narrow viewing range of light-emitting atoms in the plasma, but the particular viewing point in the plasma can be easily adjusted which can optimize detection limits for some elements.

The axial orientation of the torch is a horizontal position with the plasma pointed to the optical path of the instrument and the viewing point is centered in the middle of the torch's plasma. This orientation is viewing a longer path of elemental

emission in the plasma and thus "views" greater emission intensity of elements improving detection limits (Tyler and Goldstone, 2003). This difference in viewing point has its advantages and disadvantages (Tyler and Goldstone, 2003). The axial orientation has a sensitivity advantage in analyzing simple, clean samples, with minimal dissolved organics and suspended colloidal solids. This advantage can vary anywhere between 2-10 fold improvement in detection limits over the radial orientation. When the chemical matrix effects are minimal, the axial orientation of the torch is preferred for improved detection limits. However, the axial orientation sometimes has interference problems with samples containing high dissolved solids and complex matrix effects (Tyler and Goldstone, 2003).

The radial orientation is specifically designed to have an adjustable viewing point to avoid complications of analysis with dissolved solids over 1%. This orientation is particularly advantageous in samples where a high amount of dissolved solids are expected to be in solution. The orientation's advantage comes from its adjustable viewing point and its more robust plasma compared to the axial orientation's plasma. The robust plasma of the radial orientation promotes less interference and may provide more accurate data in complex matrix samples. The ability to adjust the viewing point of this torch allows the analysis to be focused on a particular emission point in the plasma, rather than the total emission length of the plasma in the axial orientation (Tyler and Goldstone, 2003). Note the improvements in detection limits of the axial torch orientation compared to the radial orientation for many elements in Table 1.5 adapted from Tyler, 1994.

Table 1.5: Table Modified from "ICP-MS, or ICP-AES and AAS? –a comparasion" to Illustrate Improved Detection Limits with Axial Orientation (Tyler, 1994).

Element	Wavelength (nm)	Radial torch orientation detection limit (ug/L)	Axial torch orientation detection limit (ug/L)
Ag	328.068	2	0.5
Al	396.152	6	1.5
As	188.979	22	5
Ba	455.403	0.3	0.04
Ca	396.847	0.07	0.01
Cd	214.438	1.5	0.3
Cd	228.802	2.1	0.4
Co	228.616	3.5	0.8
Co	238.892	4.5	0.5
Cu	327.396	2	0.6
Fe	259.94	5	0.4
Fe	238.204	2.3	0.35
K	766.491	6.5	0.5
Mg	279.553	0.09	0.01
Na	588.992	2	0.15
Ni	231.604	2.1	0.7
Pb	220.353	25	3
Pd	340.458	12	1.5
Ti	334.941	0.5	0.13
V	292.402	3.5	0.4

With high dissolved solids samples such as seawater, the pumped sample solution is converted to a mist with a stream of argon at the nebulizer tip. The dry argon gas results in some aqueous sample evaporation at the nebulizer tip which in turn causes a salt precipitate to form and grow on the tip until it becomes large enough to break off, and then the cycle begins again. This salt particle buildup cycle at the nebulizer tip has some effect on the sample mist production, resulting in a small cyclic drift in elemental emission in the plasma as the salt precipitate develops and breaks off repeatedly. The argon humidifier option minimizes salt formation at the nebulizer tip, enhancing emission signal stability (Agilent Technologies, 2012;

Bennight, 2012), and is especially useful for high dissolved solids samples such as coastal and sea water samples.

A nebulizer is a device that rapidly changes liquid into a mist. This mist, or aerosol, is then transported from the nebulizer to the plasma in a flow of argon gas. Nebulizers for ICPs come in two types: pneumatic and ultrasonic. The most commonly used nebulizer is the pneumatic nebulizer. Pneumatic nebulizers are generally less expensive and have various models that allow optimization for specific types of samples. There are many different models of pneumatic nebulizers, but the most commonly used is the concentric nebulizer (Bennight, 2012).

The concentric nebulizer has a defined shape and function, but several types are available. For example, though trade offs exist, some perform better for high dissolved solids samples (Bennight, 2012). Concentric nebulizers have a tiny orifice ending in a fast flow of argon gas. The high speed at which argon flows past the end of the capillary tube containing aqueous sample makes a low-pressure area. This low-pressure area is where the solution is introduced to the carrier argon gas flowing at a high speed. The interaction at the low pressure-area meeting the rapid flow argon gas consequently breaks up the solution into an aerosol. The concentric nebulizer is more prone to clogging, due to its tiny orifice, but is also a reasonably sensitive and stable device (Bennight, 2012).

The concentric nebulizer may be the most common nebulizer, but it is not the most efficient. The ultrasonic nebulizer is more efficient in getting the sample into a mist for the plasma. These models have an increased fine mist production over the concentric nebulizer, and a detection limit improvement factor between 5 and 50

times better than the concentric nebulizer (Nham, 2010). Ultrasonic nebulizers maintain stability longer than concentric nebulizers and result in elemental emission intensity in the plasma more than 10 times greater than the general emission intensity for a concentric nebulizer. ICP instruments have a number of options in terms of settings to fine-tune an instrument to efficiently and accurately analyze different samples (Nham, 2010), including radiofrequency power level to plasma optimizing temperature, flow rates for cooling argon, nebulizer argon, and supplemental argon flow, signal read time, signal read replications, and other settings.

1.8 Possibility of Using Crude Oil Source Trace Metals Such as Vanadium for Tracking Plumes and Identifying Impacted Sea and Coastal Bay Sediments.

Crude oils from all over the globe are generally composed of the same hydrocarbon compounds. The primary difference between crude oils is that the ratio of these particular hydrocarbons is unique to the crude oil reservoir source, the reservoir's depth, and the time period it has remained in the reservoir (Mendelssohn et al., 2012). Crude oils have four major classes of compounds: resins, aromatics, asphaltenes, and saturates (Mendelssohn et al., 2012) and the ratio of these in a source dictate the dominant composition and chemical state of a particular crude oil. Saturate hydrocarbons dominate these groups and are usually found in most cases at the site of any given oil spill. Asphaltenes are the class of hydrocarbons that are heavy in molecular weight and predominantly contain the trace metals vanadium and nickel. It is important to note that this class is more resistant to biological degradation (Mendelssohn et al., 2012).

1.8.1 Different Crude Oil Sources Contain Highly Variable Concentrations of Vanadium

Crude oils are different in each region. This difference is usually due to the makeup of the crude oil being heavy or light or its weight, in terms of predominant molecular weight of most compounds. Vanadium is a trace element that is often an abundant metallic element in crude oil (ATSDR, 2009). This abundance is highly variable, as shown in the tables presented earlier in this review, as different regions contain different concentrations of vanadium in crude oil from that selected region. This high degree of variance in concentration is well documented and is consistent with a pattern that heavy crude oils will contain more elevated concentration levels of vanadium due to the vanadium porphyrin ring structure mentioned earlier in this review (ATSDR, 2009). Lightweight crude oils, such as Louisiana crude oil, contain lesser amounts of vanadium. Heavyweight crude oils, such as found in Venezuela, have copious amounts of heavy and other non-carbon compounds, including V, and sulfur (ATSDR, 2009).

1.8.2 Measuring Vanadium and Trace Metals in Sediments

Vanadium is a trace element that is ubiquitous in nature (Rehder, 2008). Vanadium is found to be present in phosphate rocks, soils, sediments, etc., and also found in crude oils, often as an organic complex. Vanadium is found in sediments as an insoluble trivalent or tetravalent form. The natural accumulation of extractable and potentially soluble vanadium in soils is through the processes of weathering of rocks and soil minerals where the natural chemistry of vanadium causes a shift from its trivalent form (V_2O_3) to its tetravalent form ($VOSO_4$) (ASTDR, 2009). This

conversion of tri-valent to tetra-valent vanadium increases its solubility and allows the ion to be readily available as a bacterial electron acceptor (Rehder, 2008).

1.8.2.1 Speciation of Vanadium in Crude Oil

The typical inorganic vanadium species found in minerals, soils, sediments and marine environments are in the oxidation states V^{3+}, V^{4+}, $V^{+5.}$ These oxidative states vary depending on soil or sediment physiochemical conditions. A more oxidized form of vanadium (V^{4+}) is found in sandy sediment and upland soils, and a more reduced form of vanadium (V^{3+}) can be found in clay or mud sediments (Rehder, 2008). Additionally dissolved vanadium can exist in water as V^{4+} and V^{5+}. In marine environments, V^{4+} is stable in a more moderately reduced area, while V^{5+} is more stable in an oxidized environment (Wang and Wilhelmy, 2009). If V^{4+} is found in an area, it possible that V^{5+} was reduced in a biological interaction and thus this area should contain biological activity (Wang and Wilhelmy, 2009). However, these mineral forms found in soils, sediments, and marine environments do not represent the predominant form found in crude oil.

Vanadium in young crude oils is found in vanadyl porphyrin form, while old crude oils it is found as more non-porphyrinogenic compounds (Rehder, 2008). Vanadium is one of two metals, the other being nickel, to exist in a chelated form in different crude oils (Speight, 2007). The porphyrin ring structure is similar to basic hemoglobin or chlorophyll structures. Vanadium is bound to the centric complex by the imine R-groups. Once vanadium is bound to this centric complex, it is in a porphyrin ring structure, typically similar to the ones predominantly found in crude oil.

1.9 Extraction Methods

Good recovery of potentially mobile and biologically available trace metals from sediments can be achieved by adding approximately a gram, weighted to 2 or 3 decimal places, of the dispersed, dried sediment into a 75 mL glass digestion tube, adding 5 mls of trace metal grade nitric acid, placing a glass funnel on top of the tube to facilitate reflux action of the acid, then heating at about 120 Celsius for 8 hours. Then the funnel is removed and the acid is evaporated to about 1.5 mls, diluted to 50 mls, the contents mixed and allowed to settle, usually at least overnight. Then the clear supernatant is loaded into an instrument autosampler tube and sealed with Parafilm or a plastic-lined screw cap until analysis (Hou et al., 2006).

1.10 Typical Background Vanadium Levels in Soils

Vanadium is an element commonly found at an average concentration of about 100 ppm (100 mg/kg) in the earth's crust (Fuller and Warrick, 1985). Generally there is a multitude of different minerals that host vanadium in their structure, such as roscoelite and carnotite (ATSDR, 2009).

The content of vanadium in the lithosphere is about 150 ppm with a common range in soils of 20 to 500 mg/kg and a typical concentration in soils of 100 mg/kg, depending on soil properties and the geologic materials from which soil is derived (Fuller and Warrick, 1985).

Figure 43 from Shacklette and Boerngen, depicts the concentration of vanadium, in ppm (ug/g), of surficial soil materials across the United States (Shacklette and Boerngen, 1984). There is an average frequency of all samples of 53 ug/g across the US. The western US has a high frequency of samples containing 200

ug/g or greater vanadium concentration as does indicated sites in southern Louisiana (Shacklette and Boerngen, 1984).

Figure 28 from Shcklette and Boerngen displays the concentration of nickel, in ppm (ug/g), of surficial soil materials across the United States (Shacklette and Boerngen, 1984). There is an average frequency of 13 ug/g for all samples. There is evidence of higher nickel concentrations in the west, midwest and selected states in the eastern part of the US, such as Maine and Pennsylvania. Nickel concentration also appears to be elevated in southern Louisiana compared to most sampling sites in the U.S. (Shacklette and Boerngen, 1984).

1.11 Evaluation of Sediment Vanadium Levels

1.11.1 Total Concentrations not Sufficient for Evaluating Impacted Areas

Total concentration levels for vanadium alone are not adequate for evaluating crude oil impacted areas. Total vanadium concentrations are highly variable in soils and sediments because concentration is influenced by levels in source geological materials in watersheds, and soil and sediment texture. So total vanadium or any trace metal in soils and sediments often cannot be used to determine if contamination has occurred.

Normalizing trace and toxic metal concentrations to abundant metals found naturally in soils and sediments can be a tool for identifying elevated trace and toxic metal concentrations, including vanadium.

A typical problem found in most assessments of toxic metal contamination is knowing what normal background levels should be with the intent, especially in previous years, of establishing a threshold concentration above which indicates

contamination and/or possibly a potential for biological toxicity. This threshold can provide a basis where metal concentrations can be compared to determine if a specific metal concentration is elevated in the area. Trace and toxic metal ratios with conservative elements in soils and sediments, such as aluminum and iron, indicate whether or not the trace metals concentrations represent typical concentrations or elevated concentrations. Conservative element concentrations are more uniformly variable relative to texture (sand, silt, and clay content) and organic matter content in natural processes of sediments, e.g. weathering of source rock, sedimentation, particle size segregation during erosion and stream transport, and humic material accumulation. These different sources and processes affect the background levels of trace metals and high concentration conservative metals similarly. Thus comparing ratios can be used to reduce the amount of variability in one sampling area from another sampling area where an elevated trace metal/conservative metal ratio indicates contamination (DeLaune et al., 2008).

1.11.2 Use of Trace Metal Ratios with Iron and Aluminum to Normalize Concentrations

An important part of normalization of trace metals comes from comparing trace and toxic metals with conservative elements. Identifying a controlled variable in a highly variable terrain is essential to being able to identify elevated concentrations of elements in an area, such as would occur at a contaminated site (DeLaune, et al., 2008). For example, predominantly sandy soils and sediments have little capacity for retaining trace and toxic metals or abundant conservative elements and extraction of such materials results in recovery of relatively low levels compared to fine-textured soils and sediments. Predominantly silt and clay material

have a much higher capacity to retain metals than sandy materials (Gambrell, 1994). However, ratios of trace metals to abundant conservative elements in uncontaminated soils and sediments tend to be similar over wide texture ranges. It is common within a region or watershed to find soils and sediments ranging widely in texture (sand, silt, and clay content). In addition, the naturally occurring organic material more associated with finer textured particles has a very high capacity to retain metals (Manahan, 2005). Thus there tends to be a strong correlation between extractable trace and toxic metals and abundant conservative elements with texture and organic matter content of soils and sediments.

Aluminum and iron are abundant constituents of many clay minerals. As soil and particularly clay minerals weather, some aluminum and iron are released to more chemically reactive and available forms, but tend to stay associated with the original soil and clay material. Natural levels of extractable iron and aluminum levels from typical clays are relatively high to the point that even if some of these metals were released to the area from a contamination source, it would not significantly change the aluminum and iron content. While trace and toxic metals such as cadmium, lead, copper, zinc, mercury, vanadium, and others are also naturally present in all soil and sediment minerals and are also released as minerals slowly weather, they tend to be present in much lower concentrations than iron and aluminum. Thus contamination of sediments with these trace elements can result in much greater increases in concentration relative to background levels and background ratios with conservative elements (DeLaune et al., 2008).

Background levels of extractable metals from sediments including iron and aluminum have a strong tendency to be correlated with differences in texture (more metals as particle size decreases and clay content increases) such that big differences in metals are going to be found depending on whether the extracted sediment is predominantly sand (low extractable levels), predominantly clay, or some variable mixture of sand, silt, and clay. Within a somewhat localized geological region therefore, dividing extractable trace metal (such as cadmium or copper, etc.) content by the iron and aluminum content in the same acid extract tends to produce the same ratio in uncontaminated materials across a wide range of texture. Within a region, a sediment sample with trace metal contamination tends to show a much higher trace metal: aluminum, or, trace metal: iron ratio than uncontaminated sediments independent of texture differences.

Figure 6 adapted from Delaune et al., 2008 has been adapted and presented below as Figure 1.2. Figure 1.2 illustrates several trace metal: aluminum ratios from two contaminated lake sediments in south Louisiana, Capitol Lake in Baton Rouge and Bayou Trepagnier west of New Orleans. These trace metal: aluminum ratios are compared to the center regression line based on uncontaminated sediments, and its 95% confidence limits. The regression line is from a larger subset of uncontaminated samples from the Chenier Plains, Little Lake, and others from south Louisiana. Trace metal : aluminum points above the 95% confidence limits and regression line indicate sediments may have or are likely to have been contaminated with these elements.

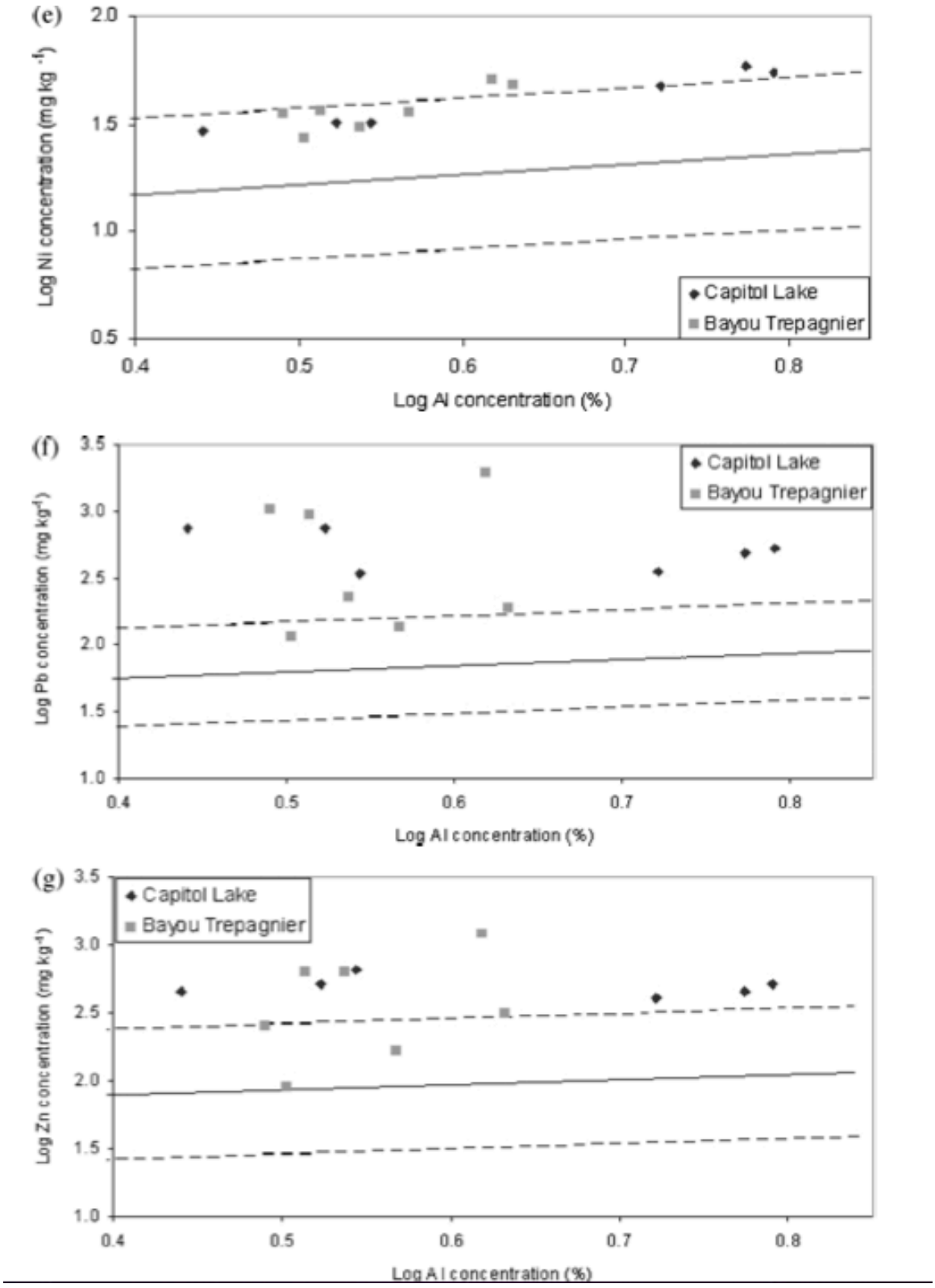


Figure 1.2: Trace Metal : Aluminum Ratios from Areas in South Louisiana
Figure adapted from Delaune et al., 2008.

Some crude oils are known to contain substantially elevated levels of vanadium and nickel. In the case of a major spill from such a crude oil, it is likely that sediments in the region will retain some of the vanadium. Unlike organic petroleum hydrocarbon compounds that have varying levels of solubility and which weather and decompose gradually but at varying rates, vanadium accumulated in sediments from a spill containing elevated vanadium should stay with the sediment for the long-term once becoming associated with it. While background levels of vanadium are also found in soils and sediments, where the common range of vanadium in soils is 20 – 500 ppm (mg/kg) and a typical concentrations in soils is around 100 ppm (mg/kg) (Fuller and Warrick, 1985), sediment materials contaminated with vanadium such as from an oil spill event, likely will have greater vanadium : aluminum and vanadium : iron ratios than uncontaminated sediments in the same region. Similarly, vanadium associated with crude oil in an oil spill plume could be elevated in the water associated with a plume for a shorter period of time. However, ratios with iron and aluminum in water would not be useful as iron and aluminum concentrations are typically very low in surface waters due to their low solubility. For water samples, comparing vanadium levels in a possible plume path with control site levels may be useful for tracking a plume for a short period of time of perhaps many hours to a few days. For water samples, vanadium ratios with abundant soluble metals like calcium and magnesium might be useful, but no work on this topic has been reported.

1.11.3 Importance of Generating Background Data for Vanadium Concentrations and Vanadium/Iron and Vanadium/Aluminum Ratios in Uncontaminated Sediments.

While there is little published information about trace metal : iron and trace metal : aluminum ratios available in crude oil sources, there is information available for V/Ni ratios in crude oil that can be used to determine crude oil presence in surface crude oil spills in sediments despite weathering that may occur to the crude oil spilled (Osuji et al., 2006). The V/Ni ratio can reflect differences in crude oil sources and the respective V/Ni distribution in crude oils (Osuji et al., 2006). Thus it stands to reason that these V/Ni ratios might be useful to track spilled crude oil in sediments and coastal systems if appropriate uncontaminated control site data are available.

1.11.4 Why Vanadium and Nickel May Increase Residual Weathered Crude Oil

Crude oil from the Macondo MC252 prospect wellhead contained V concentrations of 0.2 ppm and Ni concentrations of 1.5 ppm (Liu et al., 2012; Joung and Shiller, 2013). The concentrations of V and Ni in this crude oil are generally lower than most other Louisiana crude oils (Liu et al., 2012; Joung and Shiller, 2013). Crude oil exposed to weathering can increase concentrations of trace metals (Liu et al., 2012; Joung and Shiller, 2013). As the lower molecular weight petroleum compounds separate from the bulk of the spilled oil by volatilization at the water surface, or separation from heavier weight petroleum compounds in the water by solubility and density differences, the heavier weight residual petroleum compounds containing V and Ni subsequently contain higher metal concentrations

than the original spilled crude oil. Degradation of the lower molecular weight compounds can also be more rapid than the larger molecular weight fraction (Liu et al., 2012) contributing to a metal concentration effect. While not all crude oil sources are substantially elevated in vanadium and nickel, some are (Speight, 2007). For those that are, should a major spill occur, examining possible increases in the vanadium content of impacted sediments may be a relatively rapid and inexpensive tracking tool. However, at present, compared to other trace and toxic metals such as cadmium, lead, and mercury, there is relatively little published information on background levels of vanadium in typical coastal, near shore, and offshore sediments. Thus there is need for quantitative vanadium analyses and vanadium : iron and vanadium : aluminum ratios in the published literature for two reasons. One is to explore the feasibility of this technique as a useful tool in tracking and identifying oil spill-impacted sediments, and, the other is to serve as background information for comparing data from future possible spill data. Currently, such information is not available.

1.12 Study Objectives and Rationale

1) Conduct research on a less expensive and faster method for tracking surface and subsurface oil plumes to complement the GC/MS method
2) Establish background levels of vanadium and nickel in control site areas and areas impacted by oil

This study was based on the possibility of being able to track subsurface and surface oil plumes and identifying spilled oil impacted areas using the trace elements vanadium and nickel with vanadium : aluminum, vanadium : iron,

nickel : aluminum, and nickel : iron ratios. The goal of this study was to explore a supplemental, less expensive and faster method to track a crude oil spill using samples associated with the Deep-Water Horizon incident in 2010. However, the Macondo Prospect well (MC252) did not contain oil with substantially elevated levels of vanadium and nickel as the MC252 well contained lightweight crude oil normally lower in these elements (see Literature Review section 1.8.1). Thus the research focus was modified somewhat adding more emphasis on establishing background concentrations of vanadium and nickel in control and spill impacted sediments with their respective metal : aluminum and metal : iron ratios for possible use in future spill evaluation events where elevated levels of vanadium and nickel are present in spill oil.

CHAPTER 2

2.1 Materials and Methods

The initial experimental plan was designed to measure V and Ni associated with crude oil-impacted water and sediments with elevated vanadium and nickel concentrations. Then, to use linear regression to plot the elements V and Ni against the naturally occurring abundant elements Al and Fe where the ratios of the trace elements of interest to Fe and Al would distinguish oil-contaminated sediments from sites not impacted with oil. The literature suggests that soil and sediment Al and Fe levels are usually not affected by contamination and are useful for normalization of background levels of sediment trace metals where background levels vary with sediment texture (sand, silt, and clay) (see literature review section 1.11.2). The elements Mg and Zn were included in the sediment study as known elements that would not be high in concentration from contaminated sources for any of these sites and would act as a control test site for all statistical analyses. Magnesium is obviously elevated in seawater thus control sites and sample sites should be from similar salinity regimes.

Since it turned out the Macondo Prospect well MC252 crude oil was relatively low in V and Ni, the adjusted experimental design was based on the same normalization process, as stated above, with the goal of creating a background data set of vanadium and nickel concentrations with their respective metal : aluminum and metal : iron concentration ratios. These background data and evaluation methods may be useful for some future spill tracking. However, samples from

known impacted sites were analyzed to evaluate the approach and see if V and Ni ratios with Al and Fe in impacted sites might show trends.

2.2 Samples

Dr. John White of the Department of Oceanography and Coastal Sciences, LSU provided some samples from a site believed to be uncontaminated in the Wax Lake, Atchafalaya Bay area. These samples were important to developing a baseline for V and Ni normalization to Al and Fe.

LSU Engineering faculty donated samples from Louisiana, Mississippi, and Alabama from multiple sampling sites. Most of these samples were known to have received varying levels of contamination from the MC252 incident.

Dr. Edward Overton of the Department of Environmental Sciences, LSU donated sediment samples from suspected contaminated areas near Cocodrie, Louisiana and Barataria Bay, Louisiana. Dr. Overton also provided suspected contaminated water samples from the Barataria Bay area.

Sarah Terrebonne, former graduate assistant in the LSU Department of Biological Sciences permitted use of sediment V, Ni, Fe and Al data from the pre-spill Gulf of Mexico area. This sample set was used as representative of uncontaminated sites and similar to the Wax Lake samples. These two control sites were evaluated to look for similarity of data from unimpacted sites from different areas.

Chris Swarzenski of the United States Geological Survey permitted use of V and Ni data from water samples from various wetland areas of Louisiana, before the Deepwater Horizon oil spill.

Kim de Mutsert, a former graduate student of the Department of Oceanography and Coastal Sciences, provided water samples from oil-impacted coastal areas at the time of the spill event, but still impacted waters were not visibly apparent in the areas from which the samples were collected.

2.3 Sample Processing

2.3.1 Sediments

To ensure sediment homogeneity, all sediment samples were cleaned of large debris and mixed thoroughly in a plastic pan with a stainless steel spatula. After sediments were mixed thoroughly, they were ready for further processing which included drying, weighing into digestion tubes, acid extraction, and analyses of the diluted extracts.

Sediments were initially weighed for total wet weight before being dried at 100^{o}C for 24 hours. After the 24-hour drying period, the sediments were ground to break up any aggregates. About 1 gram of mixed dry sediment weighed to 3 decimal places was placed into a 75ml Pyrex digestion tube. The sediment was then extracted with 5ml of concentrated trace-metal-grade nitric acid at about 120^{o}C for 8 hours. Glass funnels were placed in the top of the digestion tubes to reflux the acid minimizing evaporation during the heating process, then after 8 hours, the funnels were removed and heating continued to reduce the volume of acid down to about 1.5mls. The mixture was then diluted to 50ml with deionized water. After dilution, the mixture was shaken vigorously and left to settle for 14 hours (generally overnight or longer) or until the supernatant was clear. Metal analysis was then performed on the clear supernatant by a Varian Model MPX ICP-OES.

2.3.2 Water

Water samples were filtered through a 0.45μm glass microfiber filter. The filtrate was then acidified with concentrated trace-metal-grade nitric acid until pH was adjusted to less than 2. Samples were then available for dissolved elemental analysis.

2.4 Analysis by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer)

2.4.1 Detection Limits

The ICP-OES has excellent detection limits and can measure multiple elements simultaneously (see Literature Review section 1.7.4.2). Although the ICP-OES is not as sensitive as the ICP-MS, the ICP-OES is still a powerful tool for analyzing both water and sediment sample extracts and can detect concentrations typically in the parts per billion range for multiple elements simultaneously (see Literature Review section 1.7.4.2).

2.4.2 Useful Modifications of Instrumentation

The ICP-OES used for this thesis work is based in the Department of Oceanography and Coastal Sciences at Louisiana State University (LSU) and was managed by Professor Robert Gambrell. This ICP-OES has the axial torch, humidifier chamber, and oxygen accessory AGM1 modifications. Some of these modifications were useful for improving the analyses of sediment and salt water samples in this work.

2.5 Statistics

Microsoft Excel 2010 and John's Mac Program (JMP) 10.0 were used to analyze all data. For Wax Lake sediments and pre-spill Gulf of Mexico sediments

used as control sites, a linear regression was produced with confidence limits at 95%. All other data were analyzed using the linear regression of these control sites as a baseline and using Approximated Studentized values.

Approximated Studentized values are a transformation, with a Bonferroni-adjustment, of z-score statistical method meant to emulate comparing one sample from a region with a linear relationship to a different region. The Bonferroni-adjustment (or correction) is a statistical adjustment that corrects problems associated with using multiple comparisons. By taking samples that are assumed to be uncontaminated, a linear regression was generated by comparing elements found in crude oil and comparing them to conservative elements, such as aluminum and iron, in sediment. Points outside of the confidence intervals, outliers, are considered to be elevated in concentration. Ninety-five % confidence limits were used in the linear regression graph as a measure of concentration range for typical uncontaminated sites and to compare data from possible impacted sites with the control sites. After this regression method, the formula depicted below was used in transforming given data into a residual value that could be graphed to statistically indicate if site values were truly elevated.

The Studentized value equation is shown below:

$$\text{Root Mean Squared Error} \approx \frac{(\overline{X} - \mu)}{\frac{S}{\sqrt{n}}}$$

Where $\overline{X}$ = sample mean

μ = mean of distribution

S = Approximated Standard deviation

n = number of samples

Adjusting the equation yields the Approximated Studentized value equation:

$$\text{Residual Values} = \frac{E_1 - (\hat{\beta}_1 \bullet E_o + \hat{\beta}_o)}{Root\ Mean\ Squared\ Error}$$

Where E_1 = Variable element of interest (vanadium, nickel, magnesium, zinc)

$\hat{\beta}_1$ = approximation of aluminum in control site regression

E_o = aluminum for given data site

$\hat{\beta}_o$ = estimated intercept value in control site regression

The formula takes into account the regression generated from the control site, Wax Lake (or pre-spill GoM) and possible impacted sites, then calculates how these possible impacted sites compare with the control, uncontaminated sites.

Figures 3.4 – 3.19 in the Results and Discussion section are similar visuals of a linear regression (solid line) of a background site with confidence limits (dotted lines) for the purpose of comparing uncontaminated sites with suspected contaminated sites. Following the linear regression graphs is a histogram depicting Approximated Studentized values with a Bonferroni-adjustment. The critical value of the z-score, shown on the x-axis, in these figures has been adjusted from 1.96 to 2.5, this change is the Bonferroni adjustment and is important to control the approximations made in the histogram graphs (Cosella and Berger, 2002). As a result, data points, depicted above the histogram bars, displays the sum of how many data points were at this score, where a score of 2.5 or greater is considered to

be a point with an elevated trace metal concentration. Figure 2.1 and the accompanying explanation illustrates the parts of the histogram plots in detail.

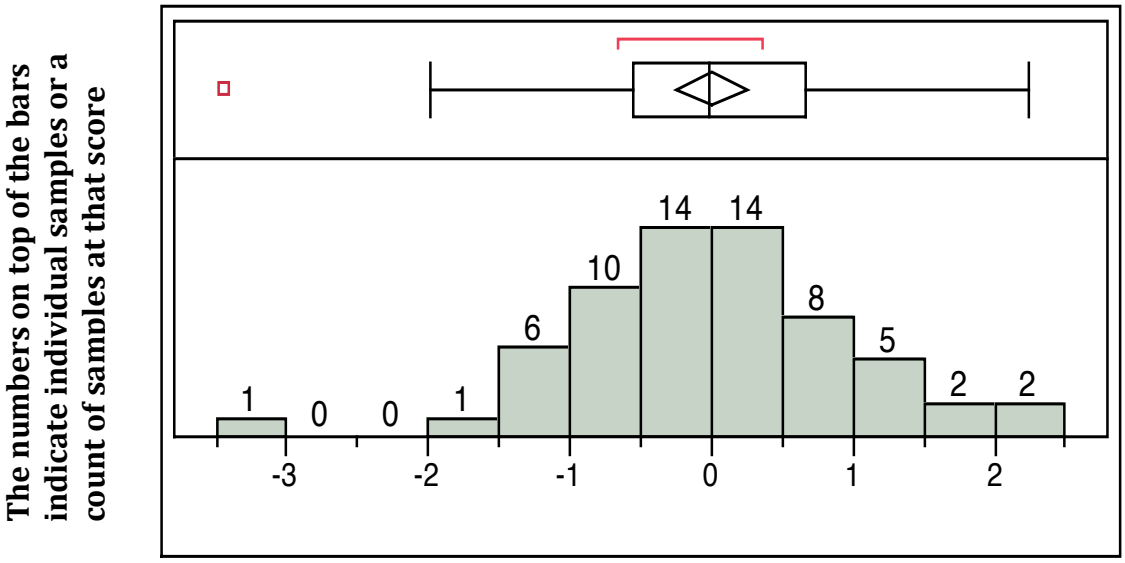


Figure 2.1: Approximated Studentized Values of Wax Lake.

The box above the histogram indicates the majority of samples at a specific area. The red line indicates the highest range of counts of the bars. The two lines connected to this box are the estimated range of samples. The symbols outside of these lines (eg. the red box to the left) are specific to the site (illustrated in the legend) and appear outside of the lines as outliers from that specific site.

Finally, a table is included that contains the data's statistics and tests, including the multiple regression analysis and ANOVA table.

The other statistical approaches used were the multivariate regression, Proc Reg Procedure in SAS, and ANOVA tables for Figures 3.4 – 3.19. All contain a similar formula that can show, on average, how elevated a certain site is when compared to

a baseline site, represented by the variable control site Intercept. This formula model is based on simple linear regression with intercept shifting to show variance in concentration of elements through intercepts. It is assumed that the X and Y, conservative element and element of interest respectively, will share a similar relationship across different sites varying in texture and thus it will further enable statistical methods to be developed to compare background levels of metals of interest to conservative elements, such as aluminum and iron (Eaton, 2005; Cosella and Berger, 2002).

Equation:

$$Y = XB_o + B_1 + B_2 + B_3 + B_4$$

Where Y = a given element of interest (V, Ni, Mg, etc.)

X = a conservative element (Al or Fe) for any site.

B_o = slope

B_1 = Baseline intercept (level adjustment for baseline)

B_2 = Barataria Bay intercept

B_3 = Cocodrie intercept

B_4 = Louisiana, Mississippi, and Alabama intercept

Differences in the intercepts will reveal differences in element ratios and therefore show if an area is statistical significance in element ratios when compared to the baseline site.

The parameter estimate field is important because it is the regression equation for predicting a dependent variable, V, Ni, Mg, and Zn, from the

independent variable, Al and Fe. Thus the intercept for the control site is a starting point for understanding if the site in question is indeed elevated or not elevated by the parameter estimate data for said site. If there is elevation at a specific site, the site will have a more positive parameter estimate or a concentration that is above the Intercept for the control site. If a concentration is not elevated, a site will have a more negative parameter estimate or a lower concentration than the Intercept for the control site. Another important factor mentioned in the ANOVA table is the significance or critical Pr > [t] value which is Pr > 0.05. Points above 0.05 are considered to be statistically insignificant and points below this value are considered to be statistically significant.

CHAPTER 3

3.1 Results and Discussion
3.2 Element Relationships in Soils and Sediments

The linear relationship between a conservative element and a non-conservative element demonstrates how conservative elements may be used in determining areas with elevated levels of non-conservative elemental concentration. Normalization of vanadium, nickel, magnesium, and zinc to iron and aluminum yields a linear regression. This regression allows for other points from suspected contaminated sites to be compared to indicate possible contamination.

3.3.1 Vanadium and Nickel Versus Aluminum and Iron in Background Soils and Sediments

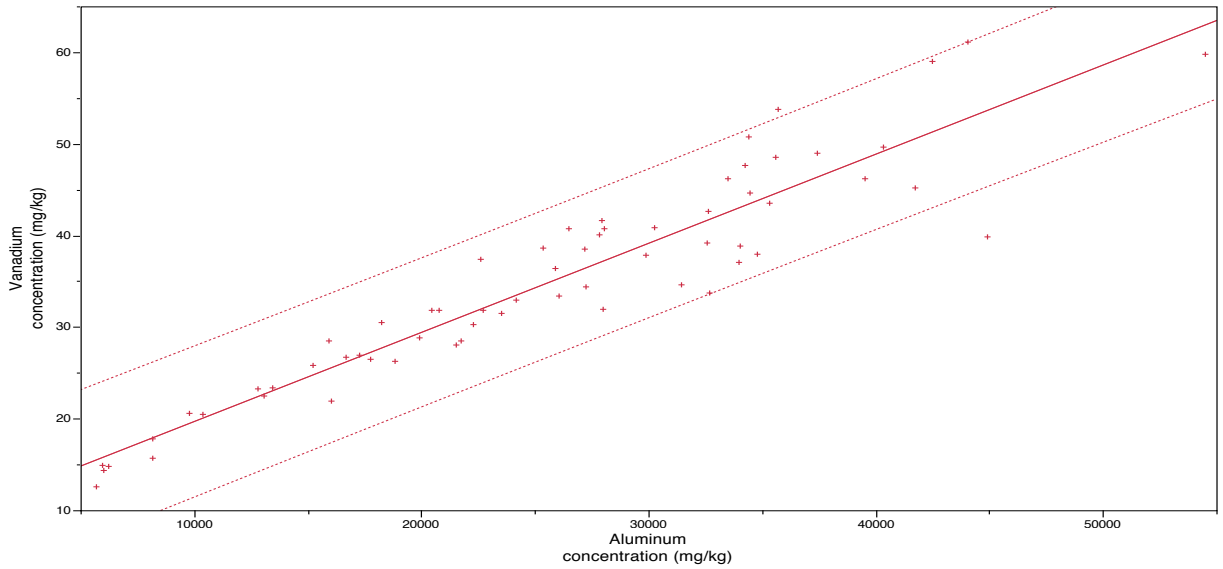
The two sites chosen for background conditions, Wax Lake and an area of the Gulf of Mexico (pre-spill), offer a different linear regression and statistical output (Figure 3.1 and 3.2). Wax Lake and pre-spill Gulf of Mexico (GoM) samples are, for the purposes of this research, considered to be uncontaminated by crude oil. The purpose behind producing a linear regression for these sites is to compare these background control sites with sites that are considered to be contaminated or possibly contaminated by crude oil, and either support or reject the hypothesis that V/Fe, V/Al, Ni/Fe, and Ni/Al ratios can be used as a means to detect elevation of V and Ni concentrations in a crude oil-contaminated area.

When sediment V and Ni were compared to Fe and Al in several figures from Section 3.3.1, there were notable differences in predictability (R^2) and trace element to conservative element ratios. Figure 3.1 revealed that V/Fe ratios are typically higher than V/Al ratios due to Fe found at a slightly lower concentration than Al.

Based on regression coefficients, the predictability of V/Al is more reliable as a linear fit than V/Fe (Figure 3.1a and 3.1b). However, Figure 3.1 also showed that Ni/Fe has a higher regression coefficient than Ni/Al. Ni/Fe ratios were also found to be at slightly lower values than Ni/Al, thus making Ni/Fe ratios a bit higher than Ni/Al ratios (Figure 3.1c and Figure 3.1d). These figures are all statistically significant and also establish a pattern of regression coefficients, as described below. This pattern is consistent throughout Figures 3.4-3.11 and Tables 3.1-3.3.8.

The linear regression lines of Wax Lake area samples and pre-spill Gulf of Mexico area samples were chosen to display in each graph as control sites (Figures 3.1 and 3.2). Additionally, the two control sites were compared to each other with respect to V/Fe, V/Al, Ni/Fe, and Ni/Al. In this comparison it is apparent that there are also similarities to these two control sites with respect to their confidence intervals. The control sites were combined and have joint confidence limits shown in Figure 3.3. It is clear that these two control sites may have a similar relationship as the samples from one control site can be found within the confidence intervals of the other site though with some difference in the slope. Samples from Barataria Bay, Cocodrie, and the north Gulf of Mexico area of Louisiana, Mississippi, and Alabama (LA/MS/AL) were analyzed and compared to the control sites (Figures 3.4 – 3.19).

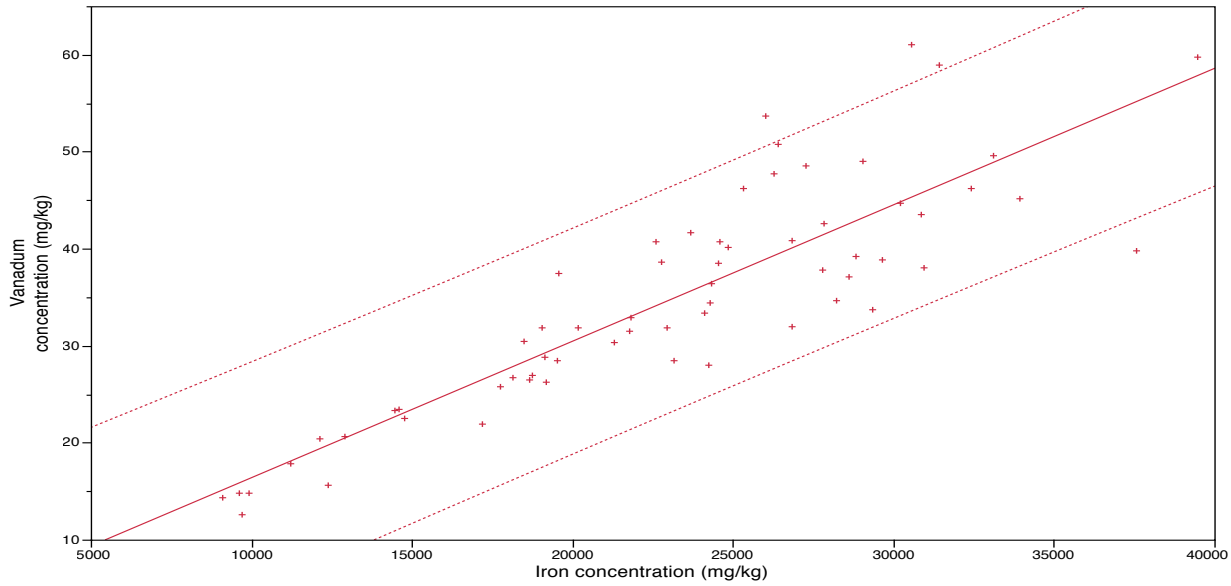
a) V vs Al



Wax Lake $V = 9.954 + (9.725 \times 10^{-4})(Al)$ $R^2 = 0.878$ $P < 0.0001$

Individual confidence intervals at 95%

b) V vs Fe

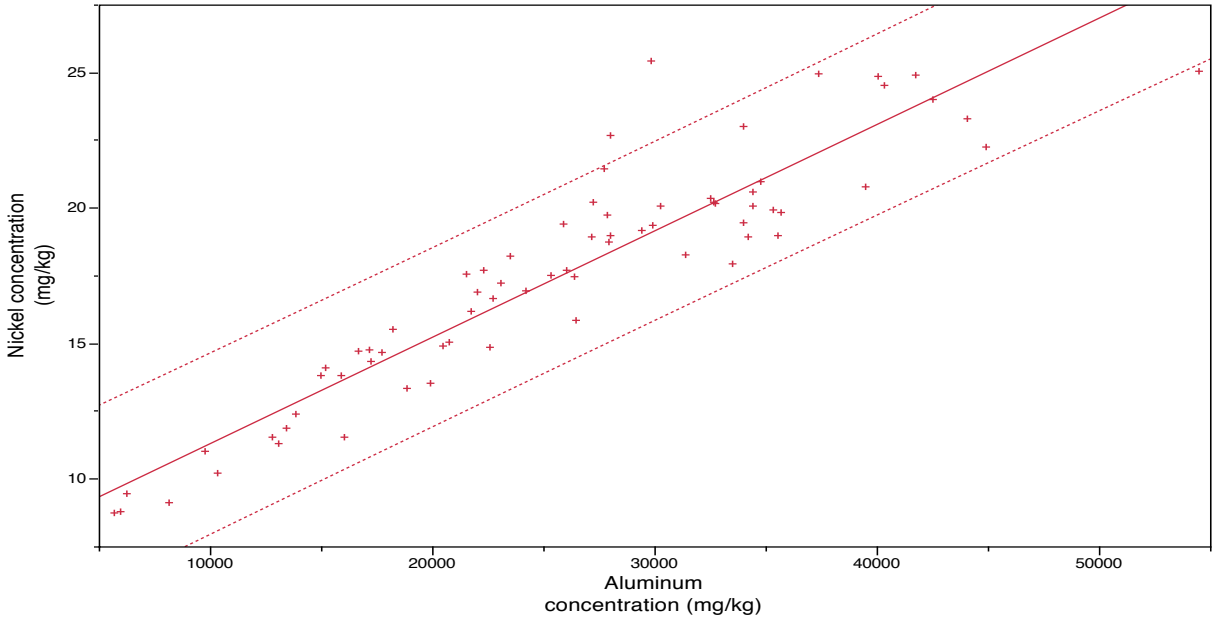


Wax Lake $V = 2.311 + (1.406 \times 10^{-3})$ (Fe) $R^2 = 0.750$ $P < 0.0001$

Figure 3.1 V and Ni Versus Al and Fe in Sediment Samples from Wax Lake

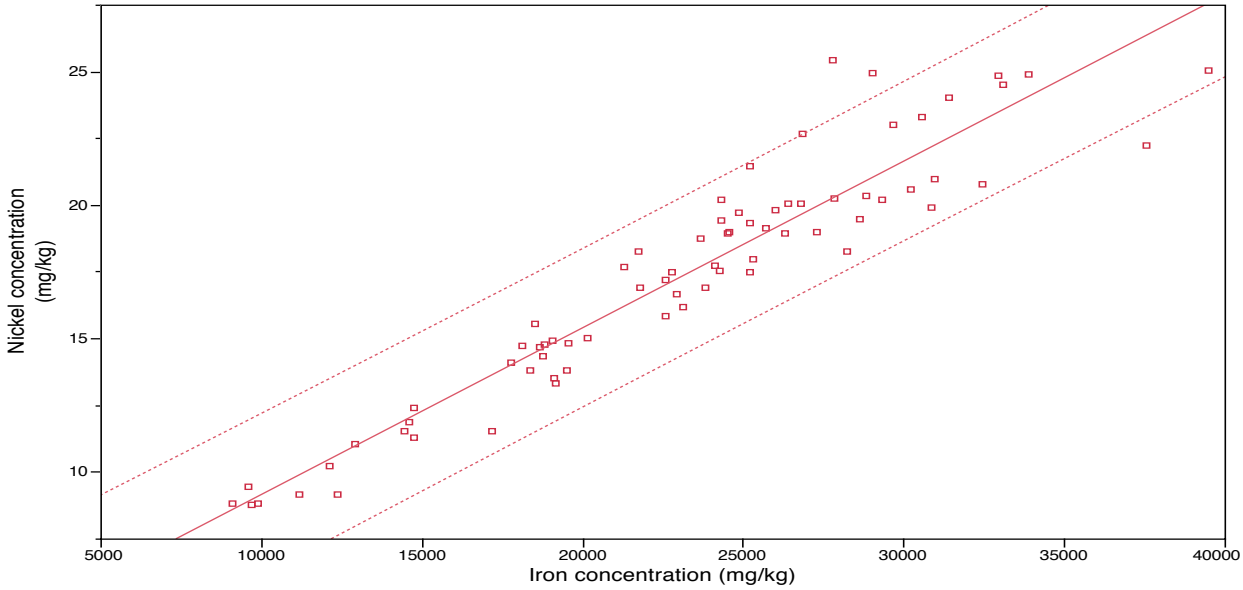
(Figure 3.1 continued)

c) Ni vs Al



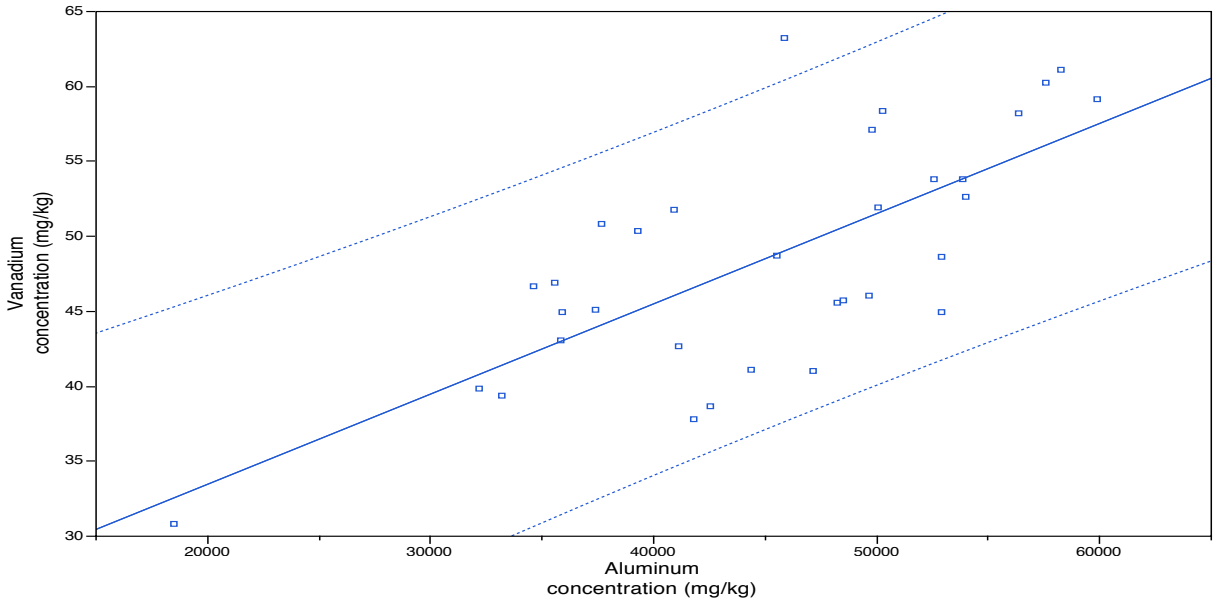
Wax Lake $Ni = 7.357 + (3.927 \times 10^{-4})\ (Al)$ $R^2 = 0.867$ $P < 0.0001$

d) Ni vs Fe



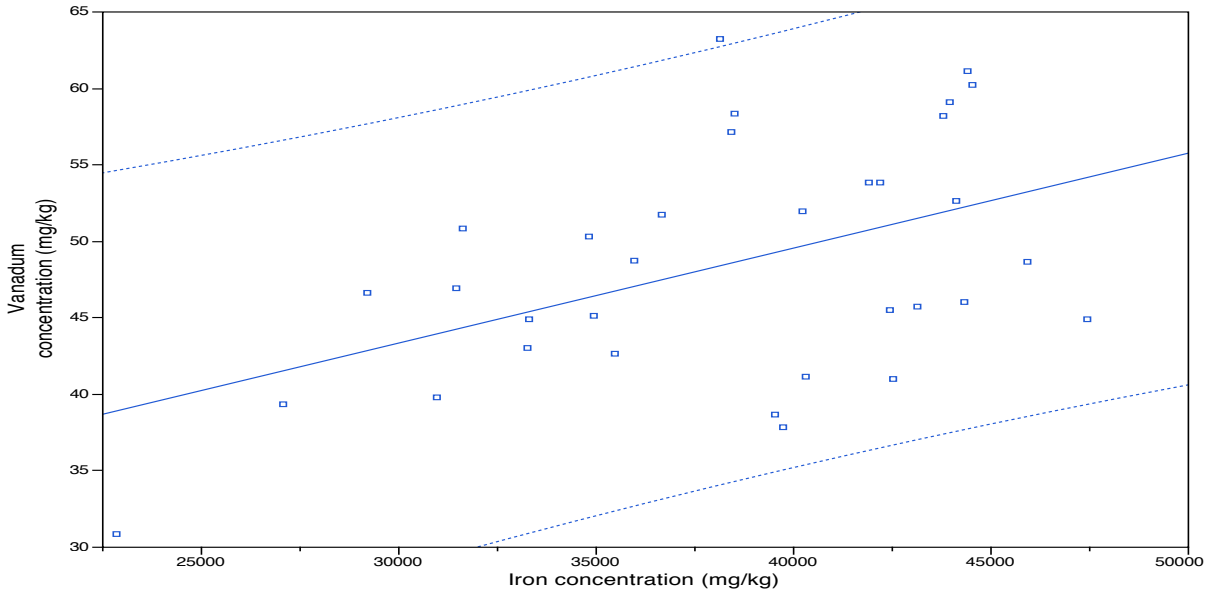
Wax Lake $Ni = 2.897 + (6.244 \times 10^{-4})\ (Fe)$ $R^2 = 0.893$ $P < 0.0001$

a) V vs Al



Pre-spill GoM $V = 21.37 + (6.018 \times 10^{-4})(Al)$ $R^2 = 0.511$ $P < 0.0001$
Individual confidence intervals at 95%

b) V vs Fe

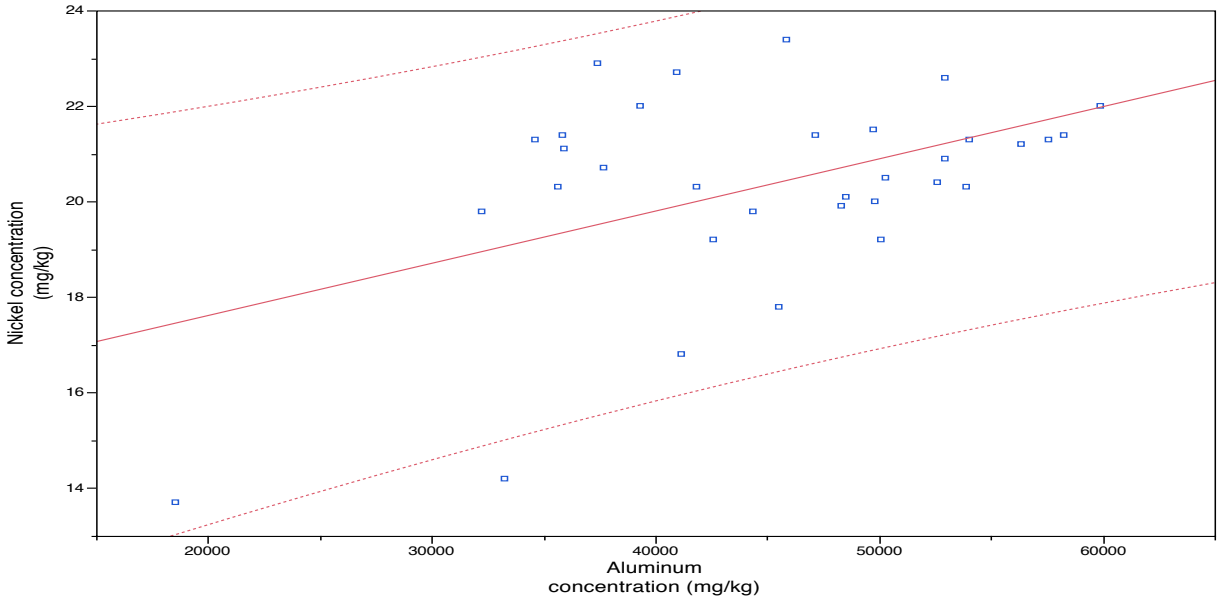


Pre-spill GoM $V = 24.68 + (6.208 \times 10^{-4})$ (Fe) $R^2 = 0.227$ $P < 0.0051$
Individual confidence intervals at 95%

Figure 3.2 V and Ni versus Al and Fe in Sediment Samples from Pre-spill GoM

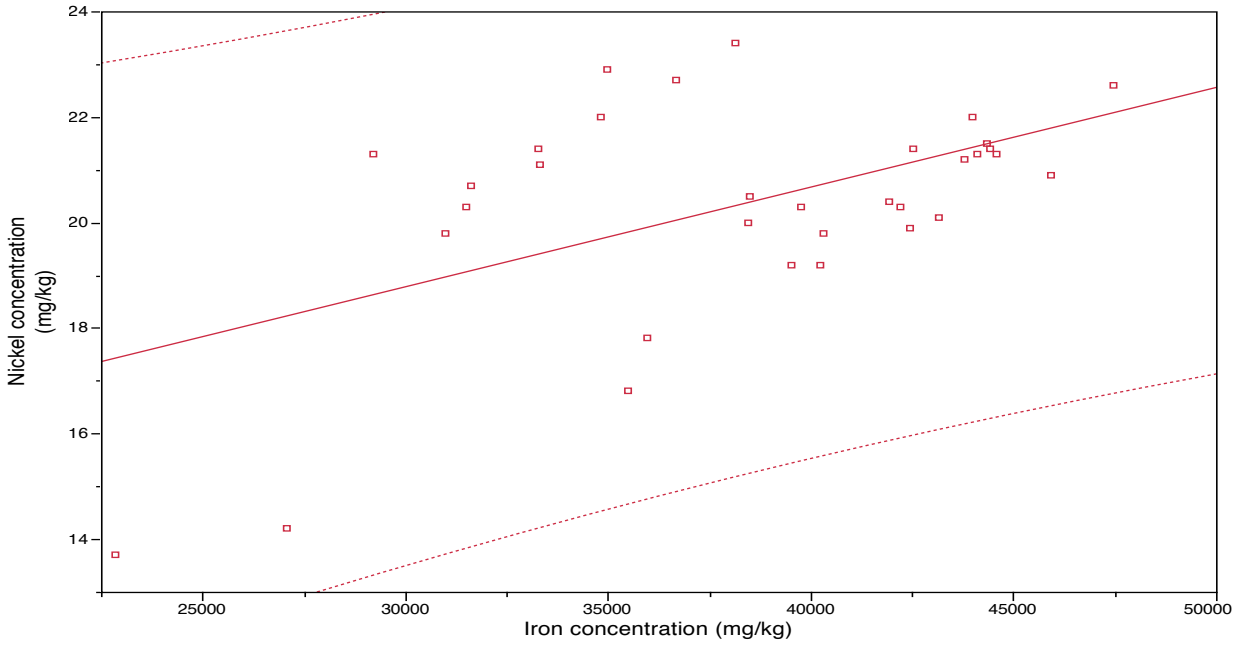
(Figure 3.2 continued)

c) Ni vs Al



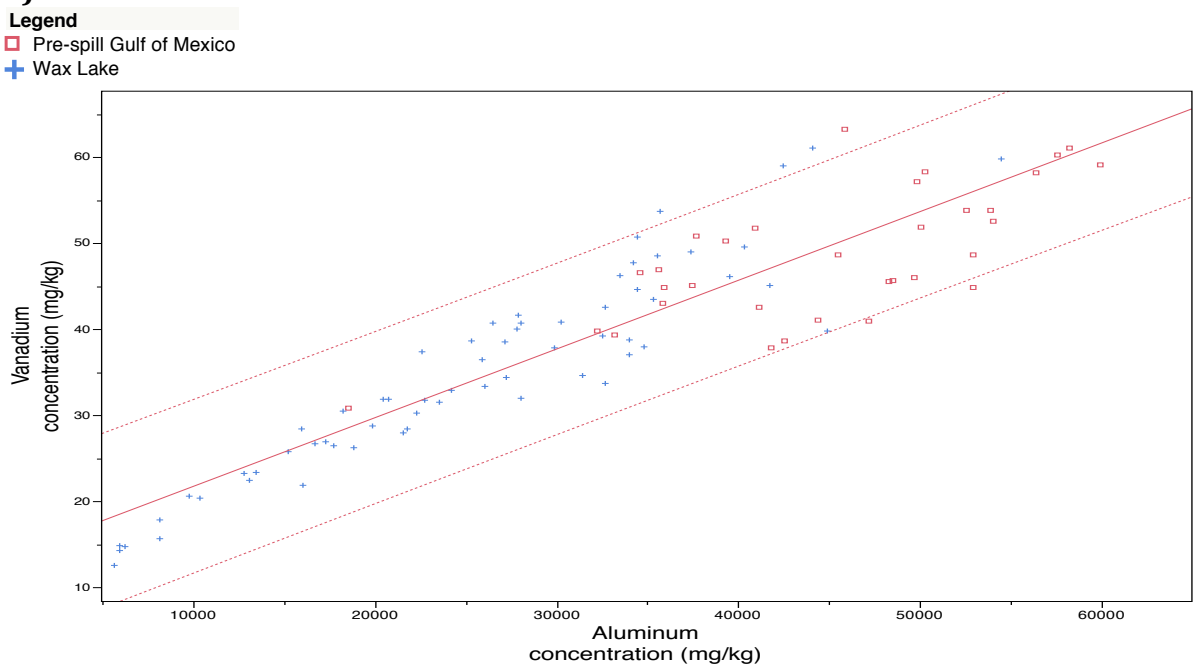
Pre-spill GoM Ni = 15.42 + (1.093 x 10^{-4}) (Al) R^2 = 0.222 P < 0.0056

d) Ni vs Fe



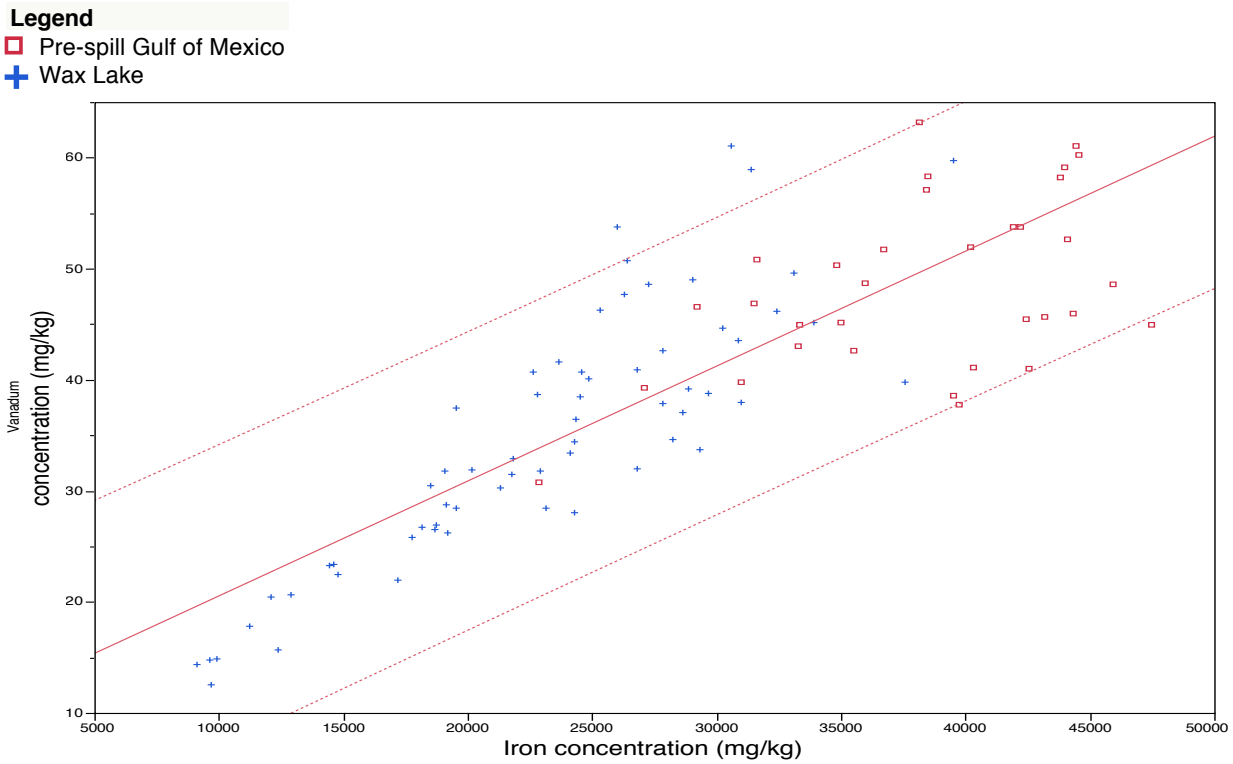
Pre-spill GoM Ni = 13.11 + (1.889 x 10^{-4}) (Fe) R^2 = 0.276 P < 0.0017

a) V vs Al



Combined control sites $V = 13.76 + (7.98 \times 10^{-4})$ (Al) $R^2 = 0.834$ $P < 0.0001$

b) V vs Fe

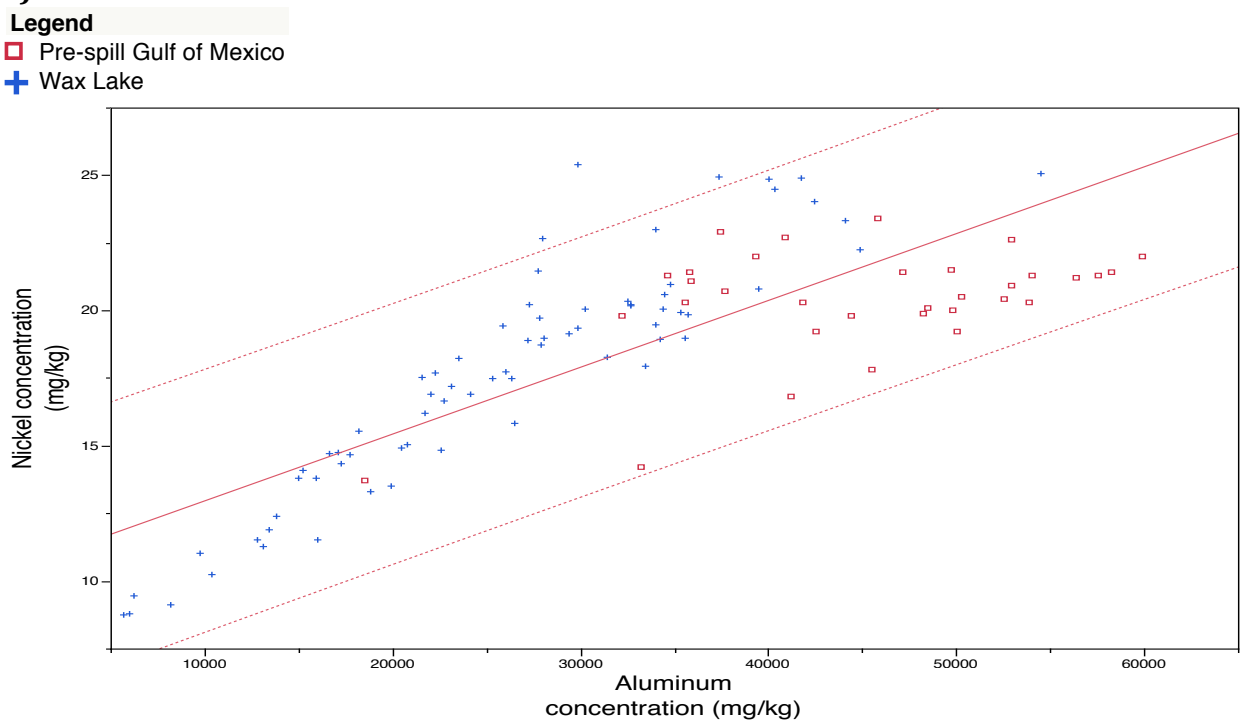


Combined control sites $V = 10.18 + (1.034 \times 10^{-3})$ (Fe) $R^2 = 0.701$ $P < 0.0001$

Figure 3.3 Wax Lake and Pre-spill GoM Comparison for V and Ni vs Al and Fe

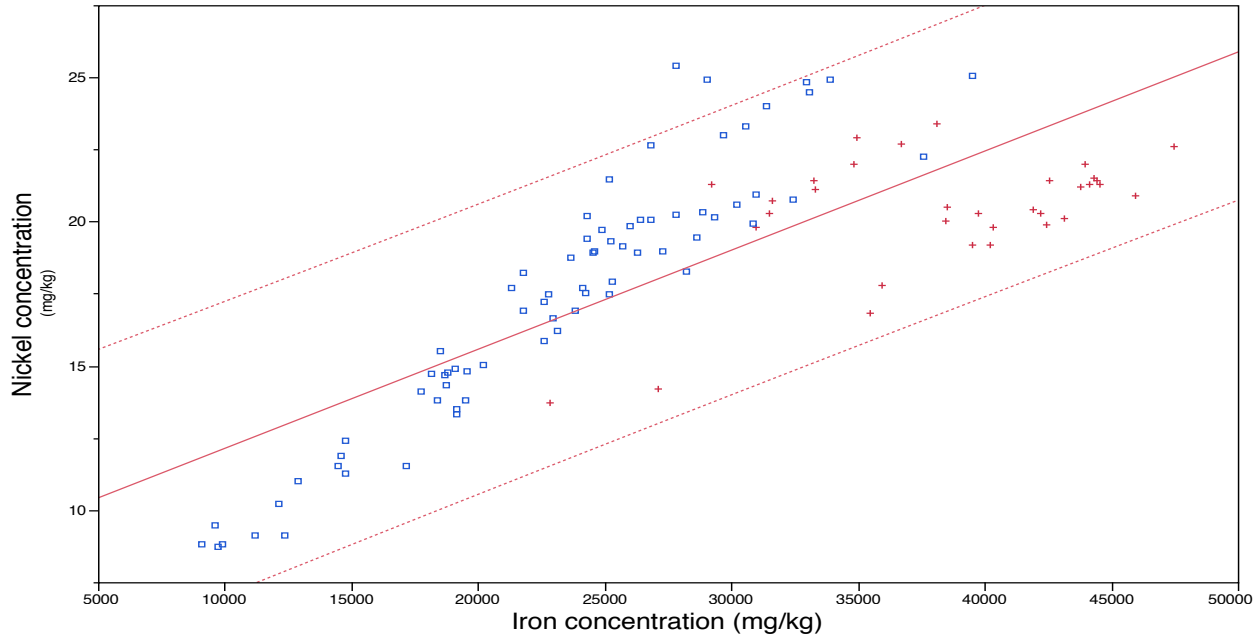
(Figure 3.3 continued)

c) Ni vs Al



Combined control sites $Ni = 10.48 + (2.47 \times 10^{-4})\ (Al)$ $R^2 = 0.664$ $P < 0.0001$

d) Ni vs Fe



Combined control sites $Ni = 8.703 + (3.434 \times 10^{-4})\ (Fe)$ $R^2 = 0.631$ $P < 0.0001$

Thus V and Ni were shown compared to the individual control sites and in the combined control sites. While the figures with the combined control sites agreed reasonably well visually, it is apparent the slopes of elements of interest versus Al and Fe were different for each control site. This work represents exploratory research in developing supplemental tracking methods. For purposes of this work, it was decided to continue the evaluation of comparing the tracking of trace metals of interest with both control sites individually looking to see what difference the different control sites may contribute.

3.3.2 Vanadium Evaluation in Areas Known to Have Contaminated Sites

3.3.2.1 V/Al Comparison to Wax Lake as a Control

Figure 3.4 and Table 3.1 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the V/Al ratios of the sample test sites using Wax Lake sediment samples as a control. The simple linear regression graph shows that several sample points from the LA/MS/AL sample set are elevated in V concentration and are outside of the confidence limits of Wax Lake control samples, but Barataria Bay and Cocodrie sites data were within the regression confidence limits (Figure 3.4a). Reviewing the Approximated Studentized values shows that LA/MS/AL has many points that scored above 2.5 (Approximated Studentized values) and support this site containing elevated vanadium concentrations (a "z-score" of greater than 2.5 explained to indicate significant elevation in Materials and Methods). Barataria Bay and Cocodrie did not score over 1.5 (Figure 3.4b). The ANOVA table shows that Wax Lake has a parameter estimate of -3.818 (This is useful to note as Wax Lake is the baseline) and

is statistically significant at P < 0.0001 (Table 3.1). LA/MS/AL has a parameter estimate of 8.312 and is statistically significant. Barataria Bay and Cocodrie are statistically insignificant with parameters estimate values of 2.166 and 4.191 (Table 3.1). Thus using Wax Lake as a control site, many of the LA/MS/AL samples indicate elevated V.

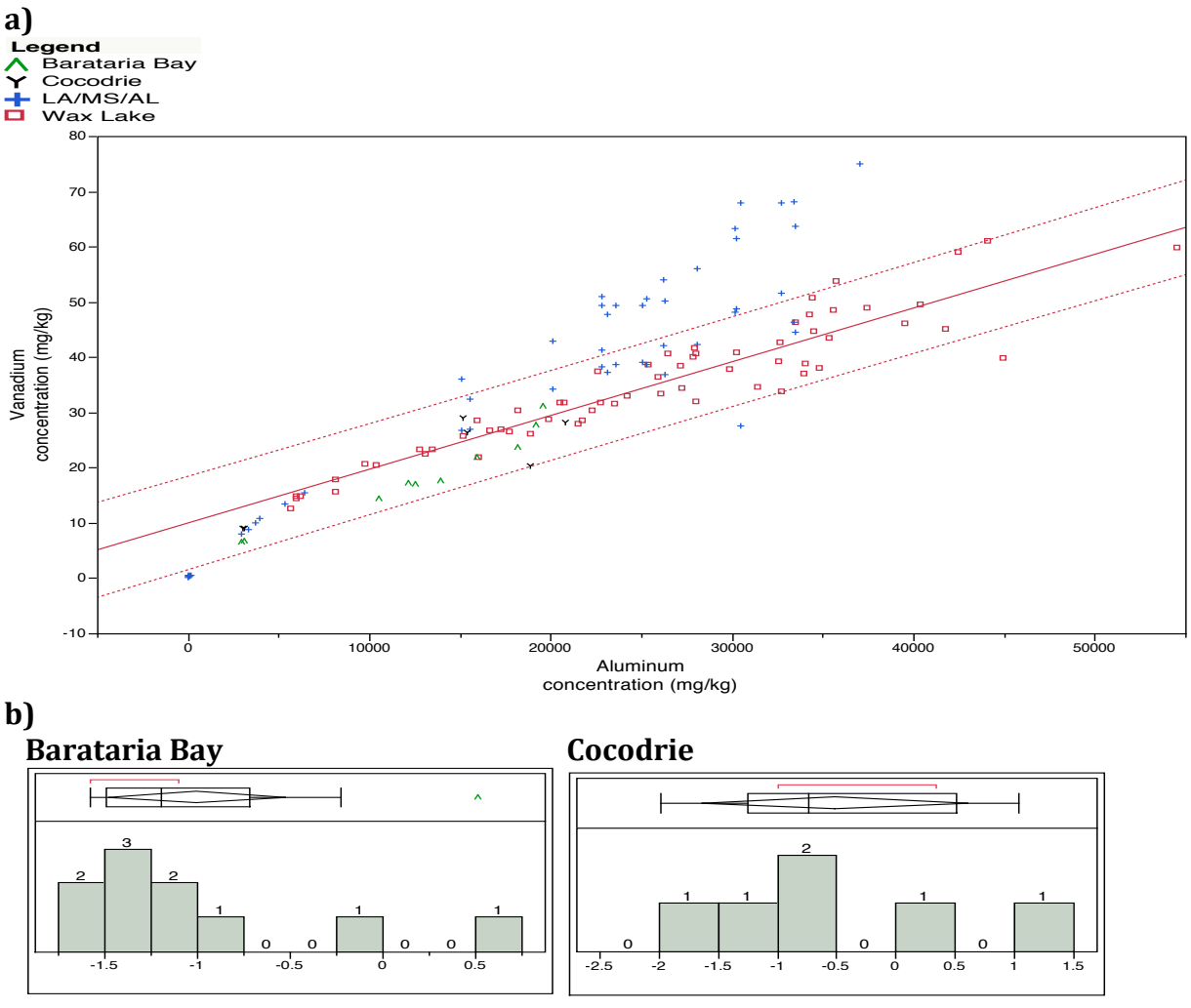


Figure 3.4 V vs Al for Sites in the Gulf of Mexico Region and Approximated Studentized Values Using Wax Lake as a Control Site

(Figure 3.4 continued)

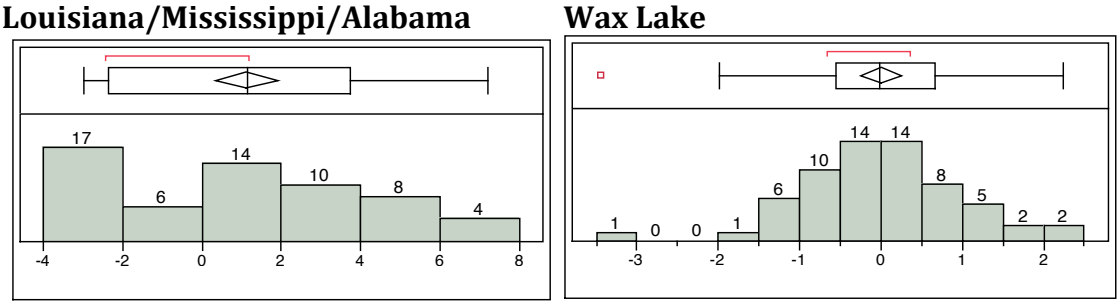


Table 3.1 V vs Al ANOVA for Sites in the Gulf of Mexico Region Using Wax Lake as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	34522	8630.40186	194.38	<.0001
Error	100	4439.84987	44.39850		
Corrected Total	104	38961			

Root MSE	6.66322	**R-Square**	0.8860
Dependent Mean	29.25935	**Adj R-Sq**	0.8815
Coeff Var	22.77296		

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Wax Lake	**1**	-3.81854	1.78833	-2.14	0.0352
AlumConc	**1**	0.00156	0.00005769	27.07	<.0001
LAMSAL	**1**	8.31246	1.53219	5.43	<.0001
BaraBay	**1**	2.16659	2.49912	0.87	0.3880
Cocodrie	**1**	4.19118	3.03509	1.38	0.1704

3.3.2.2 V/Al Comparison to pre-spill GoM as a Control

Figure 3.5 and Table 3.2 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the V/Al ratios of the sample test sites using pre-spill GoM sediment samples as a control. Using the pre-spill GoM sediment as control samples, the simple linear regression graph shows that LA/MS/AL has many points that are outside of the V/Al confidence limits of pre-spill GoM and supports elevated concentration of vanadium in the area. Barataria Bay and Cocodrie are within or under the confidence limits of pre-spill GoM (Figure 3.5a). The Approximated Studentized values shows that LA/MS/AL has multiple points that scored higher than 2.5 and supports elevated vanadium concentrations in the area. Barataria Bay and Cocodrie did not score above 1.0 (Figure 3.5b). The ANOVA table shows that pre-spill GoM is statistically significant with a parameter estimate (Intercept) of -18.15. LA/MS/AL, Barataria Bay, and Cocodrie all have parameter estimates over 15.00, with a difference of more than 20 by comparison of pre-spill GoM (Table 3.2). This large margin of difference supports that LA/MS/AL is elevated in V concentration, but the significance of Barataria Bay and Cocodrie may also mean that these sites are well under the linear regression curve and not elevated in V concentration.

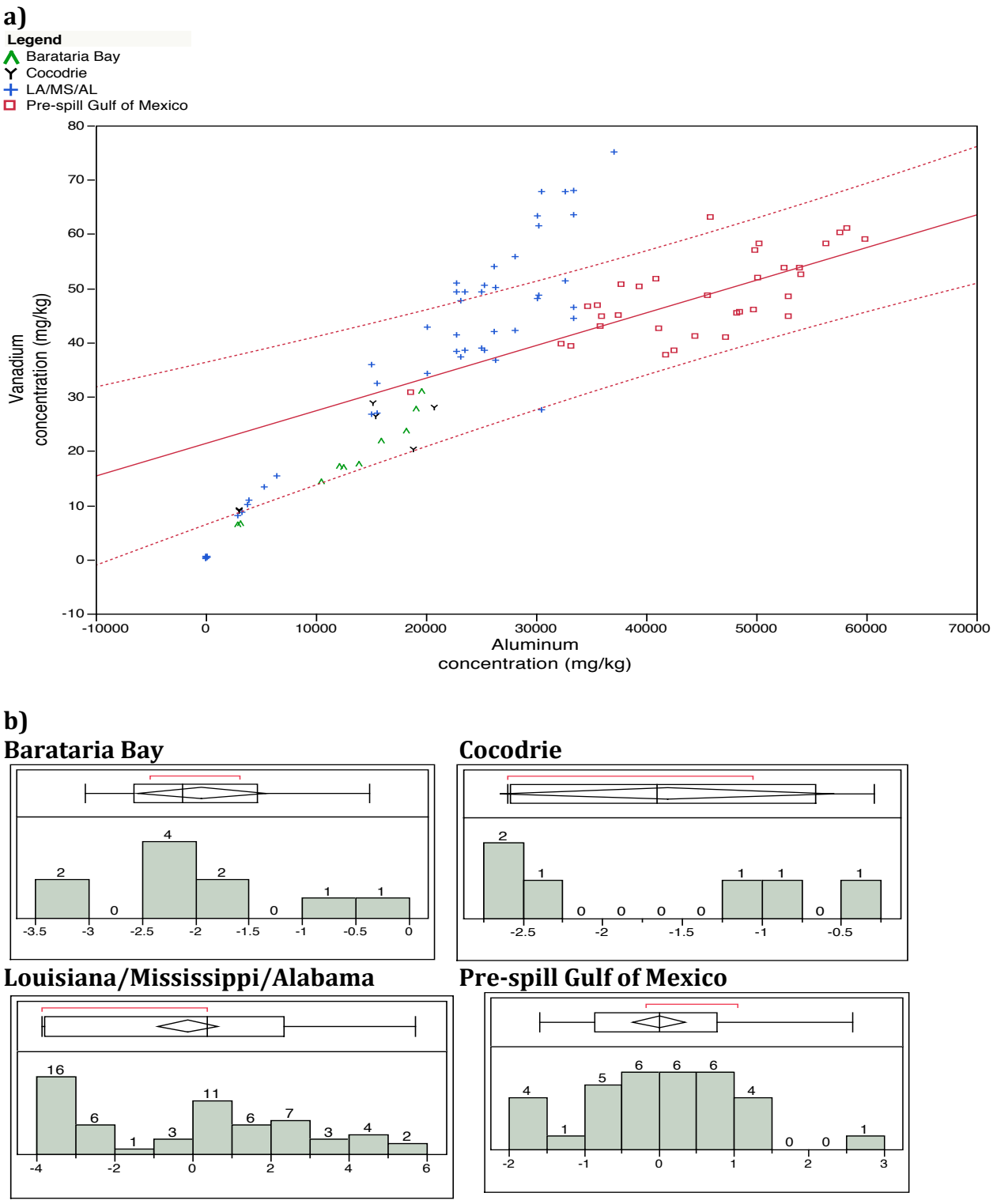


Figure 3.5 V vs Al for sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site

Table 3.2: V vs Al ANOVA for Sites in the Gulf of Mexico Region Using Pre-spill GoM as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	39800	9950.01321	155.20	<.0001
Error	103	6603.45620	64.11123		
Corrected Total	107	46404			

Root MSE	8.00695	**R-Square**	0.8577
Dependent Mean	34.45574	**Adj R-Sq**	0.8522
Coeff Var	23.23836		

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Pre-spill GoM	**1**	-18.15339	3.44059	-5.28	<.0001
AlumConc	**1**	0.00148	0.00006989	21.17	<.0001
LAMSAL	**1**	24.02733	2.62772	9.14	<.0001
BaraBay	**1**	17.53727	3.66227	4.79	<.0001
Cocodrie	**1**	19.57011	4.20907	4.65	<.0001

3.3.2.3 V/Fe Comparison to Wax Lake as a Control

Figure 3.6 and Table 3.3 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the V/Fe ratios of the sample test sites using Wax Lake sediment samples as a control. Several points on the simple linear regression graph from LA/MS/AL are elevated in concentration and are well outside of Wax Lake's confidence limits. Cocodrie has one point outside of the confidence limits. Barataria Bay has no points outside of the

confidence limits (Figure 3.6a). The Approximated Studentized values depicts that LA/MS/AL and Cocodrie have several points scored above 2.5 and support that these sites contain elevated concentrations of vanadium. Barataria Bay had no points score past 1.5 and supports this site may not contain elevated vanadium concentrations (Figure 3.6b). The ANOVA table shows that the intercept for Wax Lake shows the parameter estimate at -12.98 for the regression analysis and is statistically significant ($P < 0.0001$). The parameter estimates for LA/MS/AL and Cocodrie are 21.69 and 14.88 and are statistically significant. These parameter estimates support that the LA/MS/AL and Cocodrie sites may be elevated in vanadium when compared to the background site Wax Lake.

a)

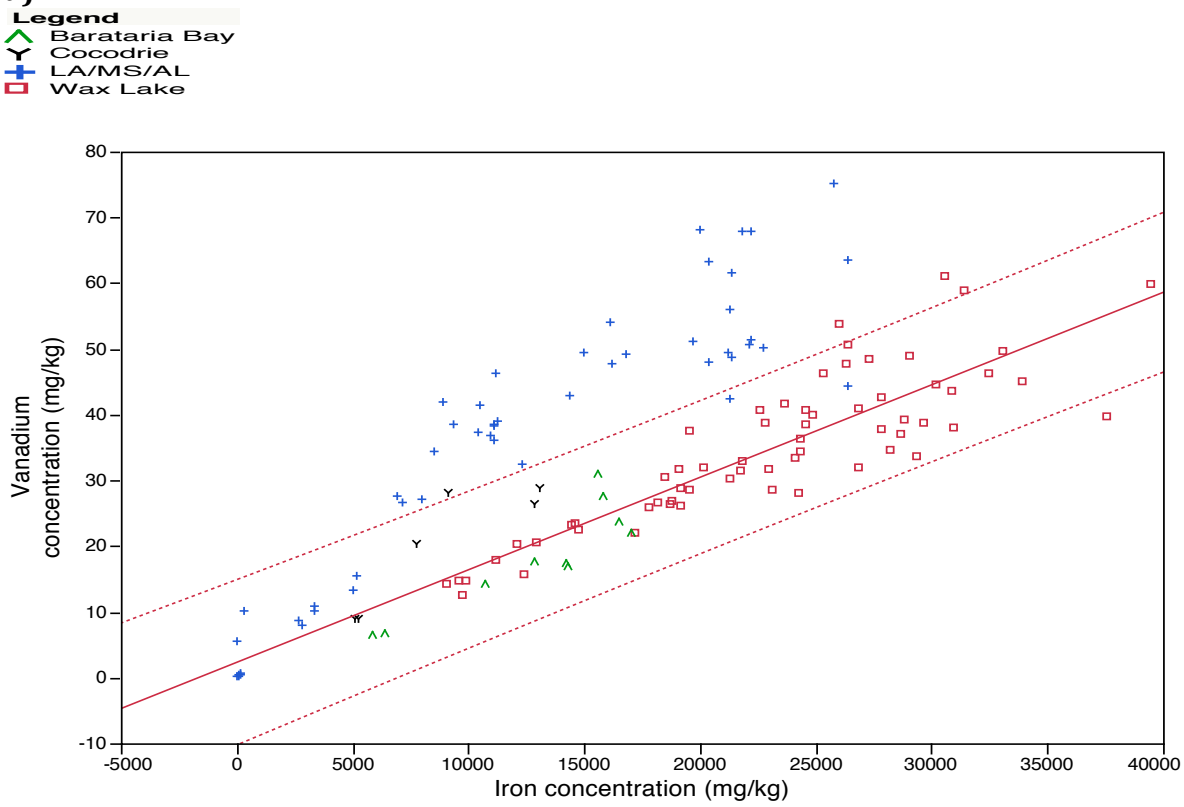
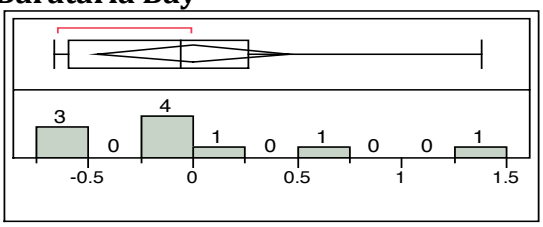


Figure 3.6 V vs Fe for Sites in the Gulf of Mexico Region and Approximated Studentized Values Using Wax Lake as a Control Site

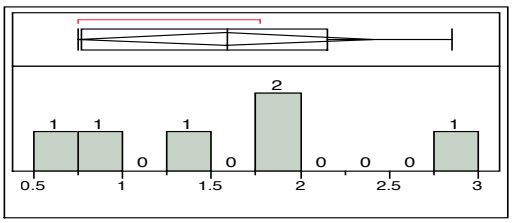
(Figure 3.6 continued)

b)

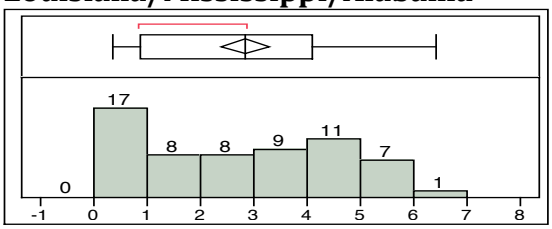
Barataria Bay



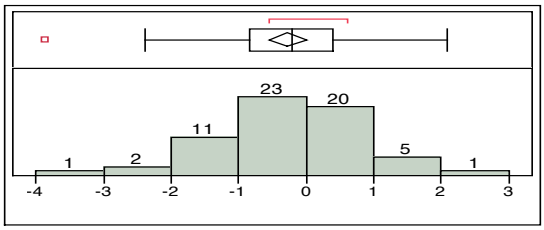
Cocodrie



Louisiana/Mississippi/Alabama



Wax Lake



However, Coodrie may have been a false positive test in the ANOVA as it is not as nearly indicative of elevation in the other two tests. Barataria Bay was statistically insignificant (P<0.0986) with a parameter estimate value of 4.57 (Table 3.3).

Table 3.3 V vs Fe ANOVA for Sites in the Gulf of Mexico Region Using Wax Lake as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	37892	9473.12043	161.16	<.0001
Error	135	7935.48314	58.78136		
Corrected Total	139	45828			

Root MSE	7.66690	**R-Square**	0.8268
Dependent Mean	30.91064	**Adj R-Sq**	0.8217
Coeff Var	24.80343		

(Table 3.3 continued)

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Wax Lake	**1**	-12.98027	2.19024	-5.93	<.0001
IronConc	**1**	0.00207	0.00008524	24.28	<.0001
LAMSAL	**1**	21.69377	1.75478	12.36	<.0001
BaraBay	**1**	4.57080	2.74865	1.66	0.0986
Cocodrie	**1**	14.87890	3.49190	4.26	<.0001

3.3.2.4 V/Fe Comparison to Pre-spill GoM as a Control

Figure 3.7 and Table 3.4 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the V/Fe ratios of the sample test sites using pre-spill GoM sediment samples as a control. The simple linear regression graph shows that several points from LA/MS/AL are elevated in concentration when compared to the pre-spill GoM regression and are outside the confidence limits. Barataria Bay and Cocodrie were displayed to be within the Pre-spill GoM confidence limits (Figure 3.7a). Looking at the Approximated Studentized values it is clear that LA/MS/AL has data points that scored above 2.5 in the Approximated Studentized values. Barataria Bay and Cocodrie did not have any scores past 0.0 and therefore are indicated to have no elevation in V/Fe concentration using pre-spill GoM baseline data (Figure 3.7b). The ANOVA table portrays that the baseline for pre-spill GoM has a parameter estimate of -33.37 for the regression analysis and is statistically significant ($P<0.0001$). Upon further testing, LA/MS/AL, Barataria Bay, and Cocodrie have parameter estimates of 41.39,

24.10, and 34.68 (Table 3.4) and are all statistically significant (P<0.0001), which is contradictory to the other graphs for Barataria Bay and Cocodrie when the comparisons being made were V vs. Fe using pre-spill GoM as a baseline. However, the ANOVA table and multivariate regression tests support these areas are all different in V/Fe concentrations when compared to pre-spill Gulf of Mexico. Other reasons for an apparent statistical difference when visual plots do not indicate contamination are given below.

a)

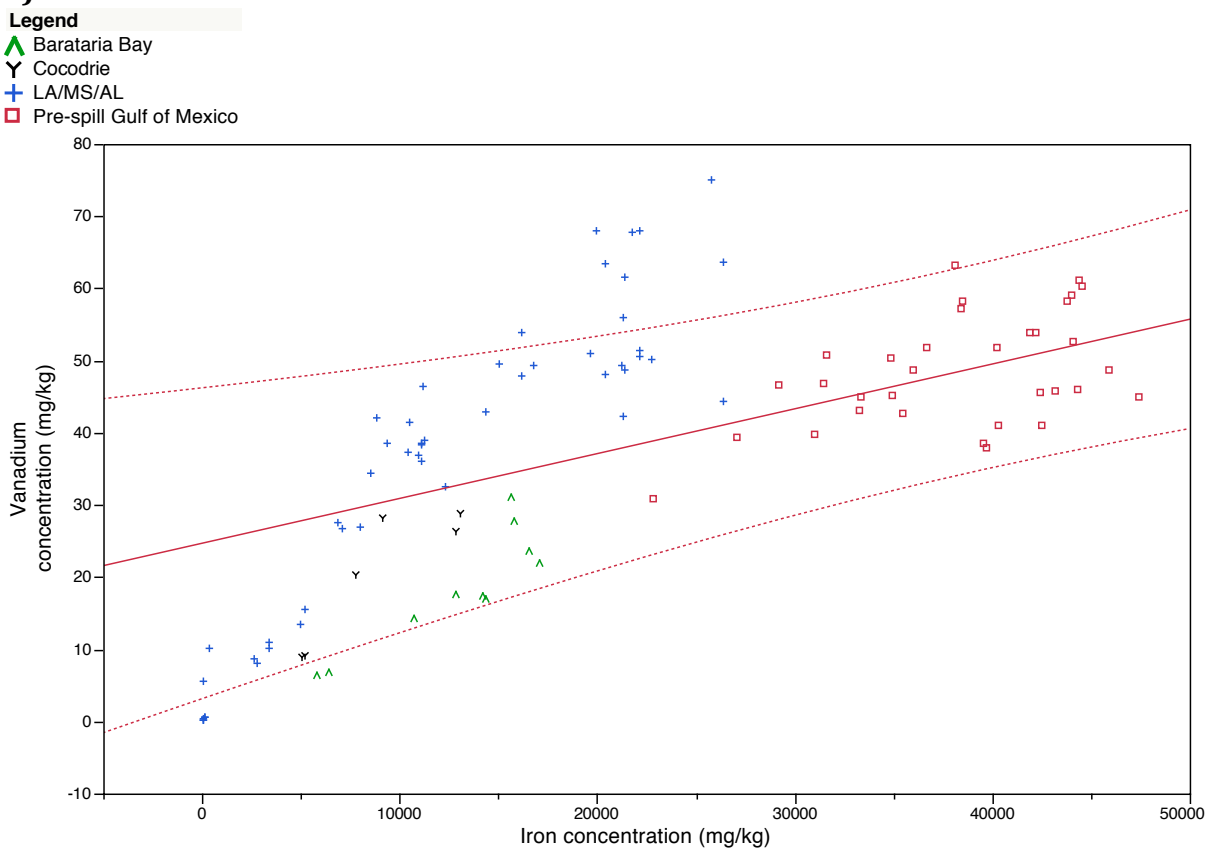
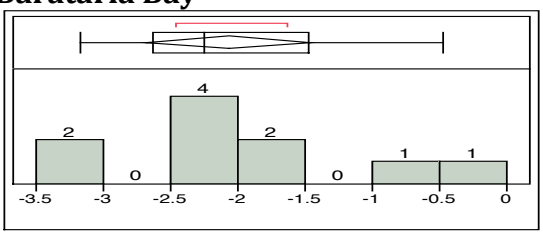


Figure 3.7 V vs Fe for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site

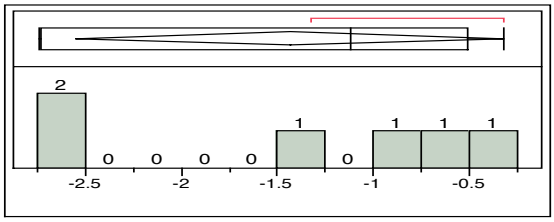
(Figure 3.7 continued)

b)

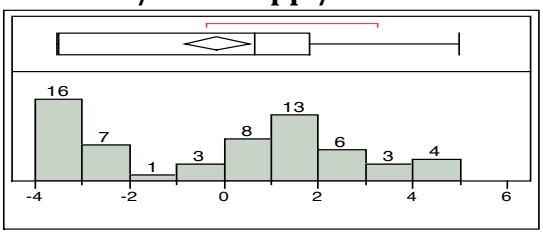
Barataria Bay



Cocodrie



Louisiana/Mississippi/Alabama



Pre-spill Gulf of Mexico

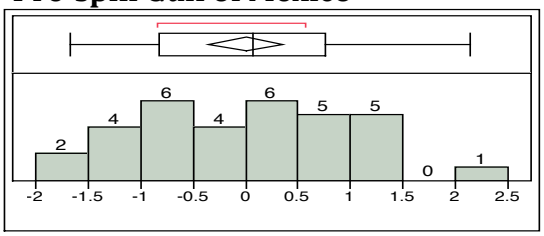


Table 3.4 V vs Fe ANOVA for Sites in the Gulf of Mexico Region Using Pre-spill GoM as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	39421	9855.33988	123.51	<.0001
Error	105	8378.17956	79.79219		
Corrected Total	109	47800			

Root MSE	8.93265	**R-Square**	0.8247
Dependent Mean	33.97161	**Adj R-Sq**	0.8180
Coeff Var	26.29445		

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Pre-spill GoM	**1**	-33.37441	4.63690	-7.20	<.0001
IronConc	**1**	0.00214	0.00011407	18.73	<.0001
LAMSAL	**1**	41.39996	3.73121	11.10	<.0001
BaraBay	**1**	24.10074	4.33139	5.56	<.0001
Cocodrie	**1**	34.68085	5.19462	6.68	<.0001

Sediment vanadium levels may sometimes be a good indicator of sites that have been exposed to crude oil (Literature Review section 1.6.2). When vanadium is compared to both aluminum and iron in Figures 3.4a, 3.5a, 3.6a, and 3.7a with sites that are suspected to contain crude oil contamination it is evident that there is elevation in concentration of vanadium levels at some of these sites. In particular, some of the LA/MS/AL samples were collected from sites with clear visual indications of Deepwater Horizon oil spill impacts. Generating data that compares two elements, one conservative and one element of interest, in an area to determine whether an area has been contaminated by crude oil can be used as a complementary test to indicate if an area should be further investigated.

Figures 3.4b, 3.5b, 3.6b, and 3.7b show that the set of samples labeled LA/MS/AL are known to have many contaminated samples, when compared to the linear regression of Wax Lake. The areas suspected of contamination were transformed into histograms that show critical values for sites. These sites are then statistically represented as samples taken from the control site Wax Lake, using the Approximated Studentized value equation.

The linear regression analysis and ANOVA table analysis displays the final tests using these data displayed in figures Table 3.1, 3.2, 3.3, and 3.4. In these tables the parameter estimate for control site intercept, Wax Lake and pre-spill GoM, is important as a it sets up a baseline to compare the suspected contaminated sites, LA/MS/AL, Barataria Bay, and Cocodrie, by parameter estimates.

The results from Table 3.2 provide support that the sites LA/MS/AL, Barataria Bay, and Cocodrie are elevated in vanadium indicating possible crude oil

contamination. Table 3.1 parameter estimates only supports that LA/MS/AL is elevated in vanadium and may contain crude oil contamination. Results from Figure 3.7 support that LA/MS/AL, Barataria Bay, and Cocodrie are elevated in vanadium based on V/Fe ratios and GoM sediment as a baseline and may contain crude oil contamination. However, upon further comparison of the simple linear regression graphs to the ANOVA tables, it becomes evident that Barataria Bay and Cocodrie sites' significance maybe due to low ratios. In this case, by not assuming all statistical significance refers to elevated concentration, it is possible that the ratios for Barataria Bay and Cocodrie may be significantly lower than the control site baseline. This argument from noting obviously low plotted trends would make the two tests agree better with one another.

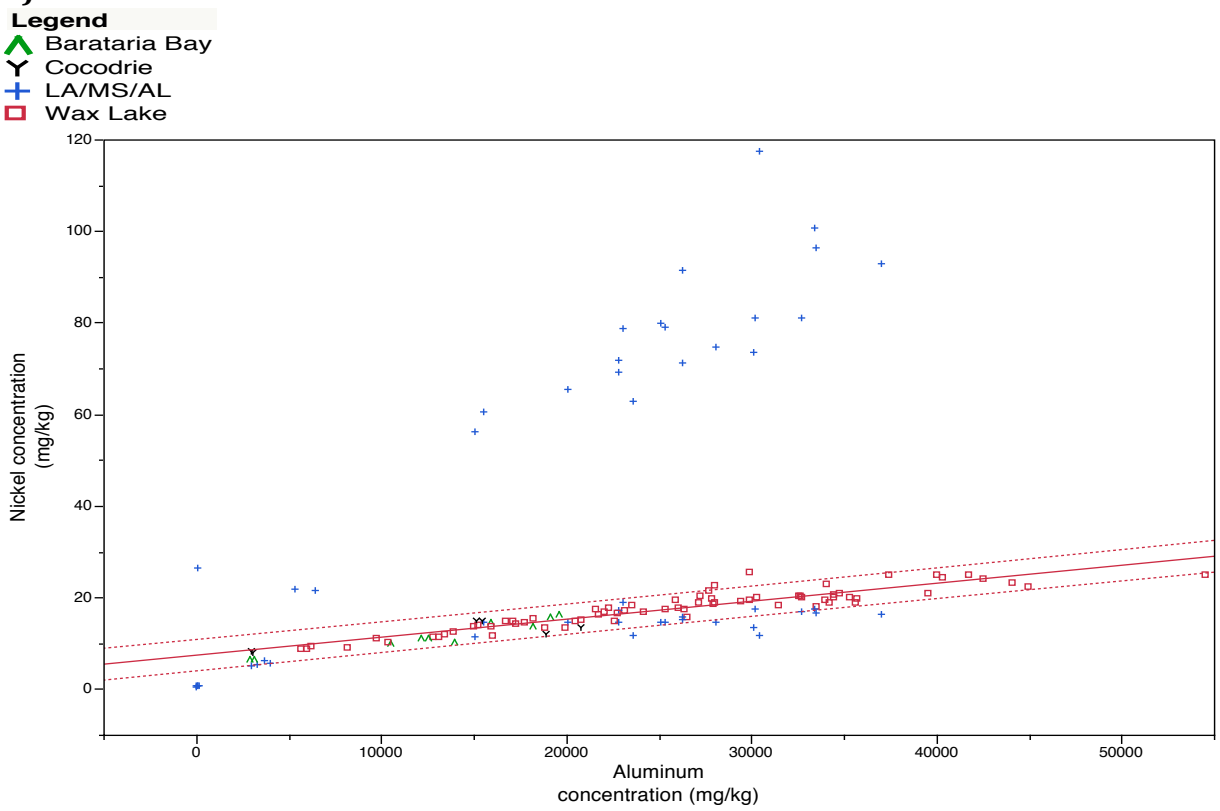
3.3.3 Nickel Evaluation in Areas Known to Have Contaminated Sites

3.3.3.1 Ni/Al Comparison to Wax Lake as a Control

Figure 3.8 and Table 3.5 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the Ni/Al ratios of the sample test sites using Wax Lake sediment samples as a control. LA/MS/AL has many points that are exceeding the confidence limits of Wax Lake by a great amount. Barataria Bay and Cocodrie have no points that are outside of the confidence limits of Wax Lake (Figure 3.8a). LA/MS/AL scored in excess of 2.5 in the Approximated Studentized value test by a large margin and is much higher than the expected values, when considering the vanadium data. Barataria Bay and Cocodrie data did not score past 1.0 (Figure 3.8b). Wax Lake has a parameter estimate of -9.328 and is statistically significant. LA/MS/AL is statistically

significant with a parameter estimate of 22.08. Barataria Bay and Cocodrie are statistically insignificant (Table 3.5). These results support elevated nickel concentration in the sample set with many visibly oiled samples and that these sites may contain crude oil contamination.

a)



b)

Barataria Bay **Cocodrie**

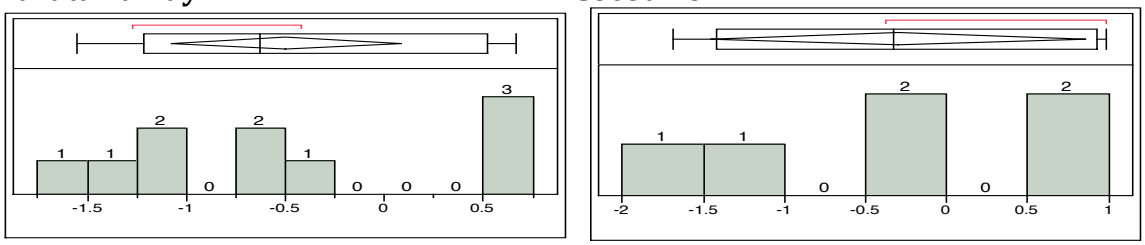


Figure 3.8 Ni vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Wax Lake as a Control Site

(Figure 3.8 continued)

Louisiana/Mississippi/Alabama **Wax Lake**

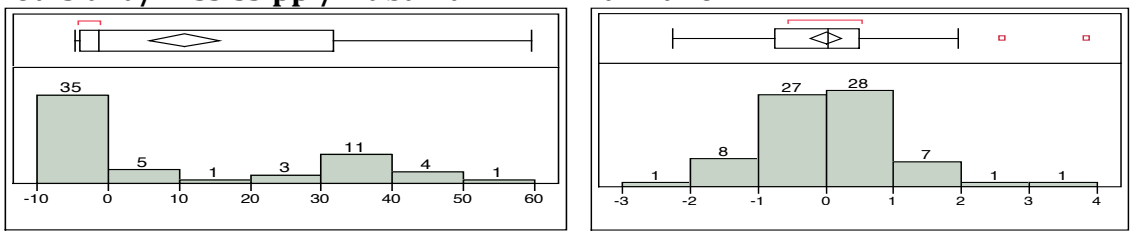


Table 3.5: Ni vs Al ANOVA for Sites in the Gulf of Mexico Region Using Wax Lake as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	29651	7412.80511	21.21	<.0001
Error	144	50322	349.45934		
Corrected Total	148	79973			

Root MSE	18.69383	**R-Square**	0.3708
Dependent Mean	22.43339	**Adj R-Sq**	0.3533
Coeff Var	83.33041		

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Wax Lake	**1**	-9.32826	4.07920	-2.29	0.0237
AlumConc	**1**	0.00105	0.00013576	7.74	<.0001
LAMSAL	**1**	22.80863	3.44177	6.63	<.0001
BaraBay	**1**	7.42962	6.52901	1.14	0.2570
Cocodrie	**1**	7.81790	8.12216	0.96	0.3374

3.3.3.2 Ni/Al Comparison to Pre-spill GoM as a Control

Figure 3.9 and Table 3.6 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the Ni/Al ratios of

the sample test sites using pre-spill GoM sediment samples as a control. Barataria Bay and Cocodrie did not have points that surpassed the upper confidence limit of pre-spill GoM (Figure 3.9a). LA/MS/AL has multiple points that scored over 20 in the Approximated Studentized values histogram well over the indicator value of 2.5, while Barataria Bay and Cocodrie did not exceed -0.5 (Figure 3.9b). The pre-spill GoM parameter estimate is -36.29 and is statistically significant. LA/MS/AL, Barataria Bay, and Cocodrie all have parameter estimates that scored over 30.00 with statistical significance (Table 3.6).

a)

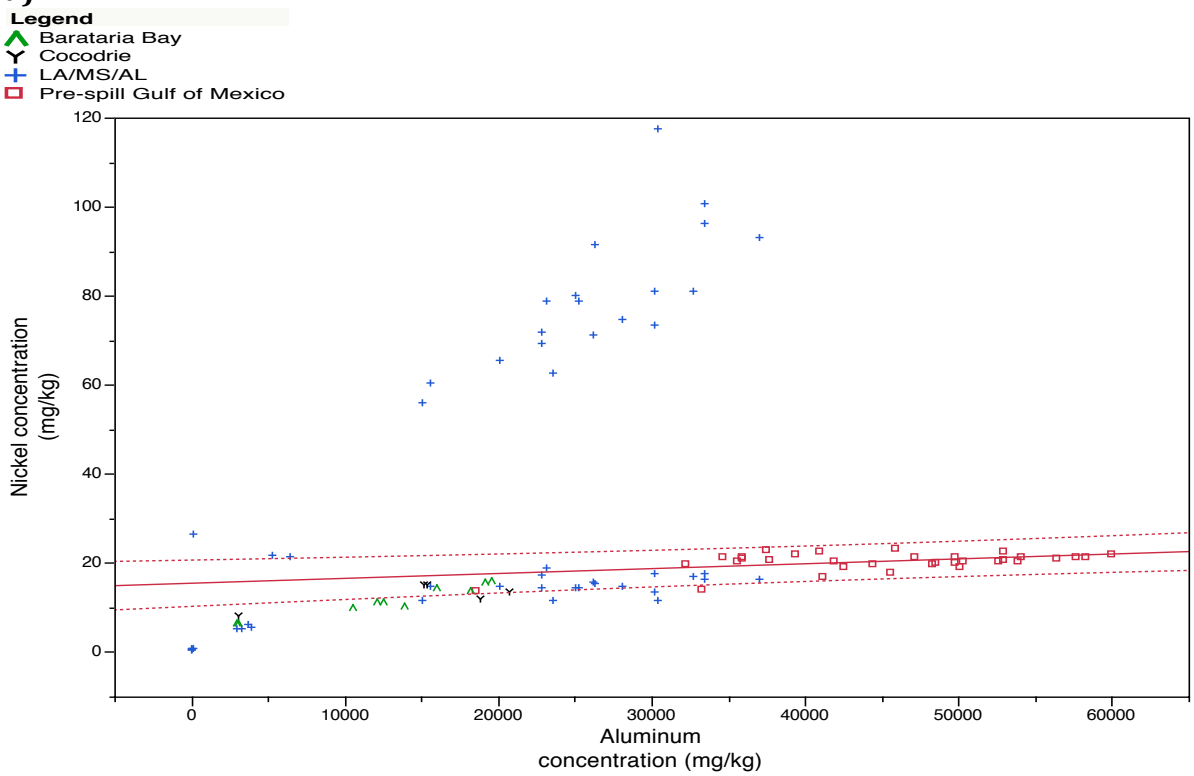
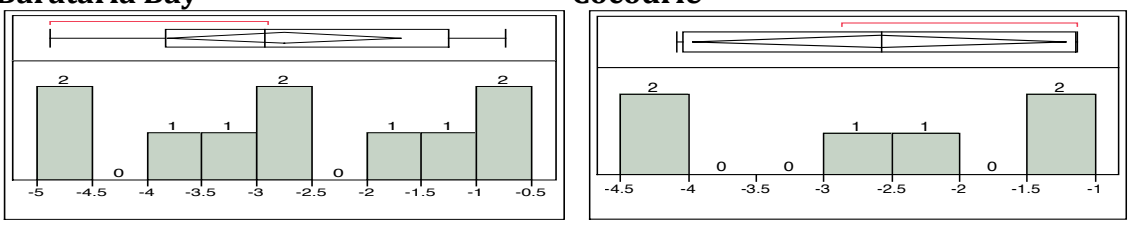


Figure 3.9 Ni vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site

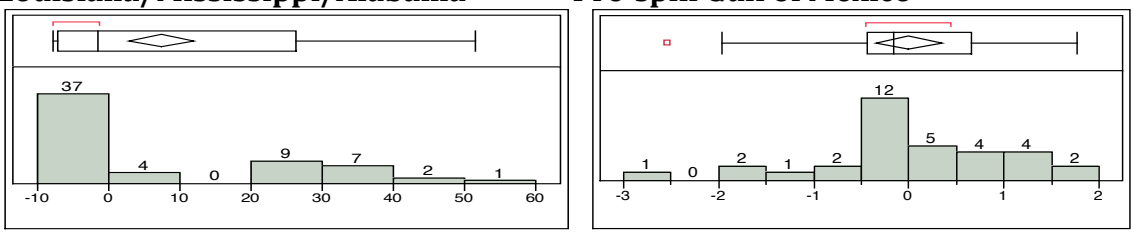
(Figure 3.9 continued)

b)

Barataria Bay **Cocodrie**



Louisiana/Mississippi/Alabama **Pre-spill Gulf of Mexico**



While the initial graphs (Figure 3.9, a and b) do not support Barataria Bay and Cocodrie being elevated in concentration, the ANOVA analysis shows that all three sites are significantly different in nickel concentration relative to the regression line of the pre-spill GoM samples.

Table 3.6: Ni vs Al ANOVA for Sites in Gulf of Mexico Using Pre-spill GoM as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	27524	6880.96589	14.75	<.0001
Error	104	48519	466.53086		
Corrected Total	108	76043			

Root MSE	21.59933	**R-Square**	0.3620
Dependent Mean	25.23028	**Adj R-Sq**	0.3374
Coeff Var	85.60876		

(Table 3.6 continued)

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Pre-spill GoM	**1**	-36.29352	9.16518	-3.96	0.0001
AlumConc	**1**	0.00126	0.00018572	6.78	<.0001
LAMSAL	**1**	46.20519	6.97317	6.63	<.0001
BaraBay	**1**	31.73968	9.82369	3.23	0.0017
Cocodrie	**1**	32.12378	11.30569	2.84	0.0054

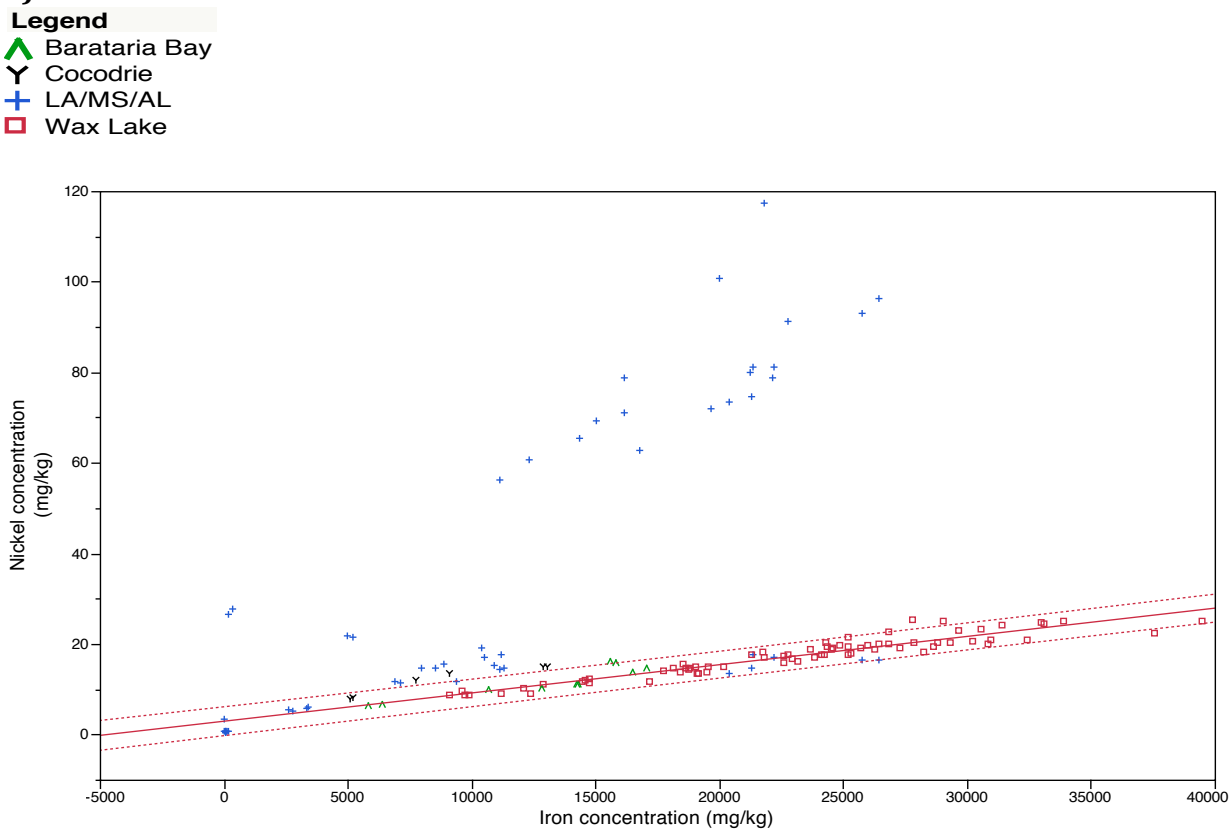
However, as noted previously, significance in the ANOVA table in this case is likely indicating most Cocodrie and Barataria Bay values are in a fairly tight pattern below the regression line, indicating in this case that significance is not indicative of elevated Ni, but lower Ni values.

3.3.3.3 Ni/Fe Comparison to Wax Lake as a Control

Figure 3.10 and Table 3.7 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the Ni/Fe ratios of the sample test sites using Wax Lake sediment samples as a control. Multiple points from LA/MS/AL, Barataria Bay, and Cocodrie are shown to be elevated in the Ni/Fe ratio and above the upper confidence limits using Wax Lake as the baseline (Figure 3.10a). Most of the data from LA/MS/AL and Cocodrie scored over 2.5 in the Approximated Studentized values, though Barataria Bay did not (Figure 3.10b). Wax Lake has a parameter estimate of -26.48 and is statistically significant. LA/MS/AL, Barataria Bay, and Cocodrie have values that exceed 30 points of difference when compared to Wax Lake individually (Table 3.7). These results have three statistical tests supporting elevated nickel concentration in

LA/MS/AL and Cocodrie.

a)



b)

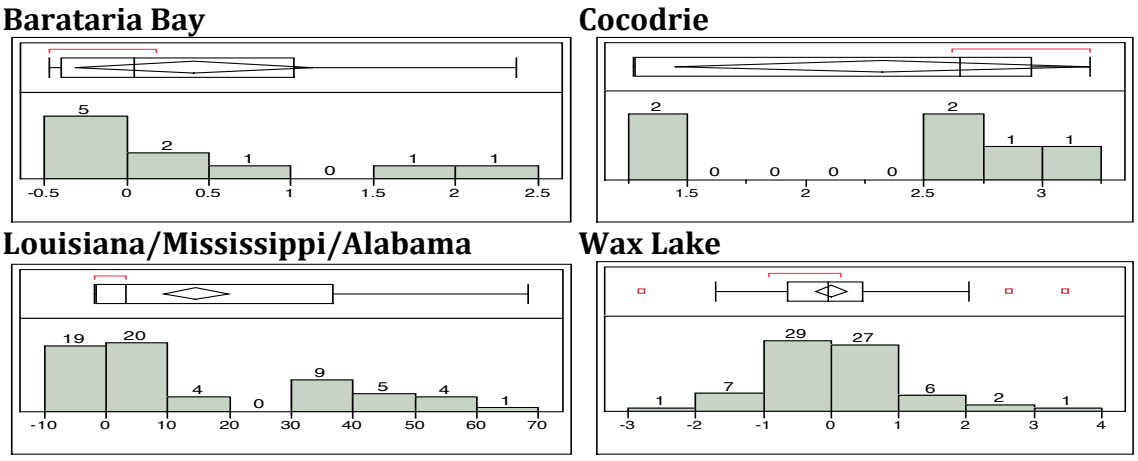


Figure 3.10 Ni vs Fe for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Wax Lake as a Control Site

Table 3.7: Ni vs Fe ANOVA for Sites in the Gulf of Mexico Region using Wax Lake as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	39099	9774.65667	34.59	<.0001
Error	146	41263	282.62260		
Corrected Total	150	80362			

Root MSE	16.81138	**R-Square**	0.4865
Dependent Mean	22.34102	**Adj R-Sq**	0.4725
Coeff Var	75.24895		

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Wax Lake	**1**	-26.48449	4.63531	-5.71	<.0001
IronConc	**1**	0.00190	0.00018175	10.44	<.0001
LAMSAL	**1**	37.47447	3.69094	10.15	<.0001
BaraBay	**1**	13.51148	5.96121	2.27	0.0249
Cocodrie	**1**	21.52679	7.59323	2.83	0.0052

3.3.3.4 Ni/Fe Comparison to Pre-spill GoM as a Control

Figure 3.11 and Table 3.8 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the Ni/Fe ratios of the sample test sites using pre-spill GoM sediment samples as a control. Multiple points from LA/MS/AL are elevated in their Ni/Fe ratio past the upper confidence limit of pre-spill GoM. Barataria Bay and Cocodrie did not exceed

the upper confidence limit and were either within or below the confidence limits (Figure 3.11a). Most of the data from LA/MS/AL scored above 2.5 in the Approximated Studentized values. Barataria Bay and Cocodrie did not score above a 0.5 (Figure 3.11b). The linear regression for pre-spill GoM is statistically significant and has a parameter value of -66.08. LA/MS/AL, Barataria Bay, and Cocodrie all scored 48.00 or more for the parameter estimate value and are all statistically significant (Table 3.8). This large difference in parameter estimates indicates that all these sites contain significantly different nickel concentrations compared to pre-spill GoM, however when this table is compared to the simple linear regression graph there is only an agreement in elevation of nickel for the LA/MS/AL site.

a)

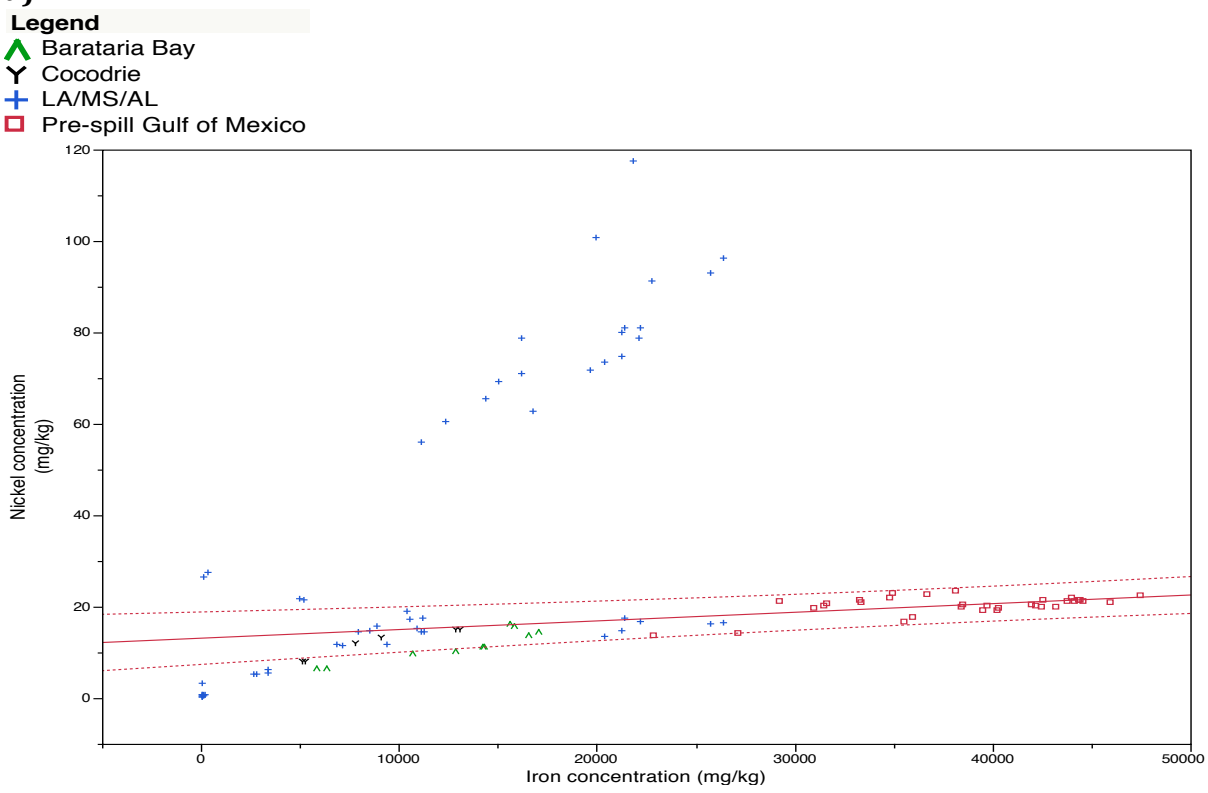
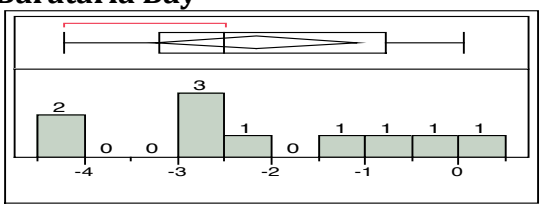


Figure 3.11 Ni vs Fe for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site

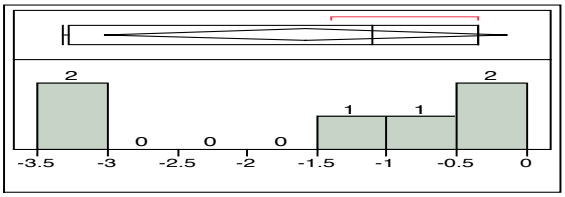
(Figure 3.11 continued)

b)

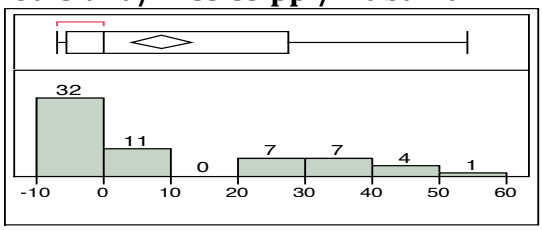
Barataria Bay



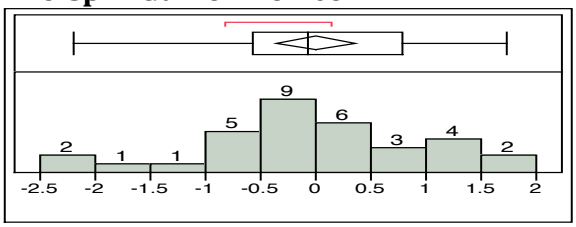
Cocodrie



Louisiana/Mississippi/Alabama



Pre-spill Gulf of Mexico



Again, it is apparent that the significance indicated in the ANOVA table for Cocodrie and Barataria Bay may be due to points for these two sites fitting a fairly linear regression line but with concentration relative to iron being consistently below the control sample regression line of the GoM samples. This finding for Cocodrie did not agree with the Ni/Fe results using Wax Lake as the control.

Table 3.8: Ni vs Fe ANOVA for Gulf of Mexico Samples Using Pre-spill GoM as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	38225	9556.36965	26.45	<.0001
Error	106	38297	361.29396		
Corrected Total	110	76523			

Root MSE	19.00773	**R-Square**	0.4995
Dependent Mean	25.05378	**Adj R-Sq**	0.4806
Coeff Var	75.86772		

(Table 3.8 continued)

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Pre-spill GoM	**1**	-66.08428	9.70329	-6.81	<.0001
IronConc	**1**	0.00226	0.00023818	9.48	<.0001
LAMSAL	**1**	73.27613	7.77445	9.43	<.0001
BaraBay	**1**	48.46301	9.14034	5.30	<.0001
Cocodrie	**1**	57.92126	10.96781	5.28	<.0001

Another sometimes-good indicator of crude oil contamination in an area is nickel (Literature Review section 1.6.2). In Figures 3.8a, 3.9a, 3.10a and 3.11a there is a distinct elevation in nickel concentration in the sample set known to have many visibly oiled samples. These sites have higher estimated values of Ni/Al and Ni/Fe based on the linear regression shown by LA/MS/AL.

The Approximated Studentized values in Figures 3.8b, 3.9b, 3.10b, and 3.11b show that most samples from LA/MS/AL reached or exceeded the critical score of 2.5 by a large amount and further support this area to be elevated based on Ni/Al and Ni/Fe ratios. Values shown for Barataria Bay and Cocodrie in these figures do not suggest that these sites were elevated in Ni/Al and Ni/Fe ratios, except for figure 3.8b which shows Cocodrie scoring above 2.5.

Tables 3.5, 3.6, 3.7, and 3.8 all depict a clear elevation of Ni/Al and Ni/Fe for LA/MS/AL with statistical significance and thus supports that these sites maybe contaminated with crude oil. Barataria Bay and Cocodrie are also shown to have an elevation of Ni/Al and Ni/Fe with statistical significance, for the exception of Table

3.5, although not as elevated as LA/MS/AL indicating possible Ni elevation, perhaps from crude oil.

Once again, as before, there is a relevant argument that ruling out the significance in the ANOVA tables meaning elevation of Ni, in the case of Barataria Bay and Cocodrie, and making the interpretation that these tables are displaying ratios that are significantly lower than the baseline results in agreement with the linear regression graphs regarding elevated concentrations or not. However, this acknowledgement introduces possible problems in the assumptions and interpretation of how control site concentrations and ratios relate to uncontaminated test sites.

3.3.4 Zinc Evaluation in Areas Known to Have Contaminated Sites

3.3.4.1 Zn/Al Comparison to Wax Lake as a Control

In the next sections, zinc (Zn) and magnesium (Mg) are evaluated as the elements of interest for testing the hypothesis regarding elements of interest being from contamination sources. There is no reason to suspect Zn and Mg contamination at any of these sites.

Figure 3.12 and Table 3.9 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the Zn/Al ratios of the sample test sites using Wax Lake sediment samples as a control. All data, except for one point from LA/MS/AL and two points from Cocodrie, is shown to be within or under the confidence limits of Wax Lake (Figure 3.12a). With the exception of one point from LA/MS/AL, there was no other data that exceeded a 1.0 score from the Approximated Studentized values histogram (Figure 3.12b). The

Wax Lake parameter estimate is 30.60 and is statistically significant. No other sites had a parameter estimate above 30.60 and all sites were statistically significant (Table 3.9).

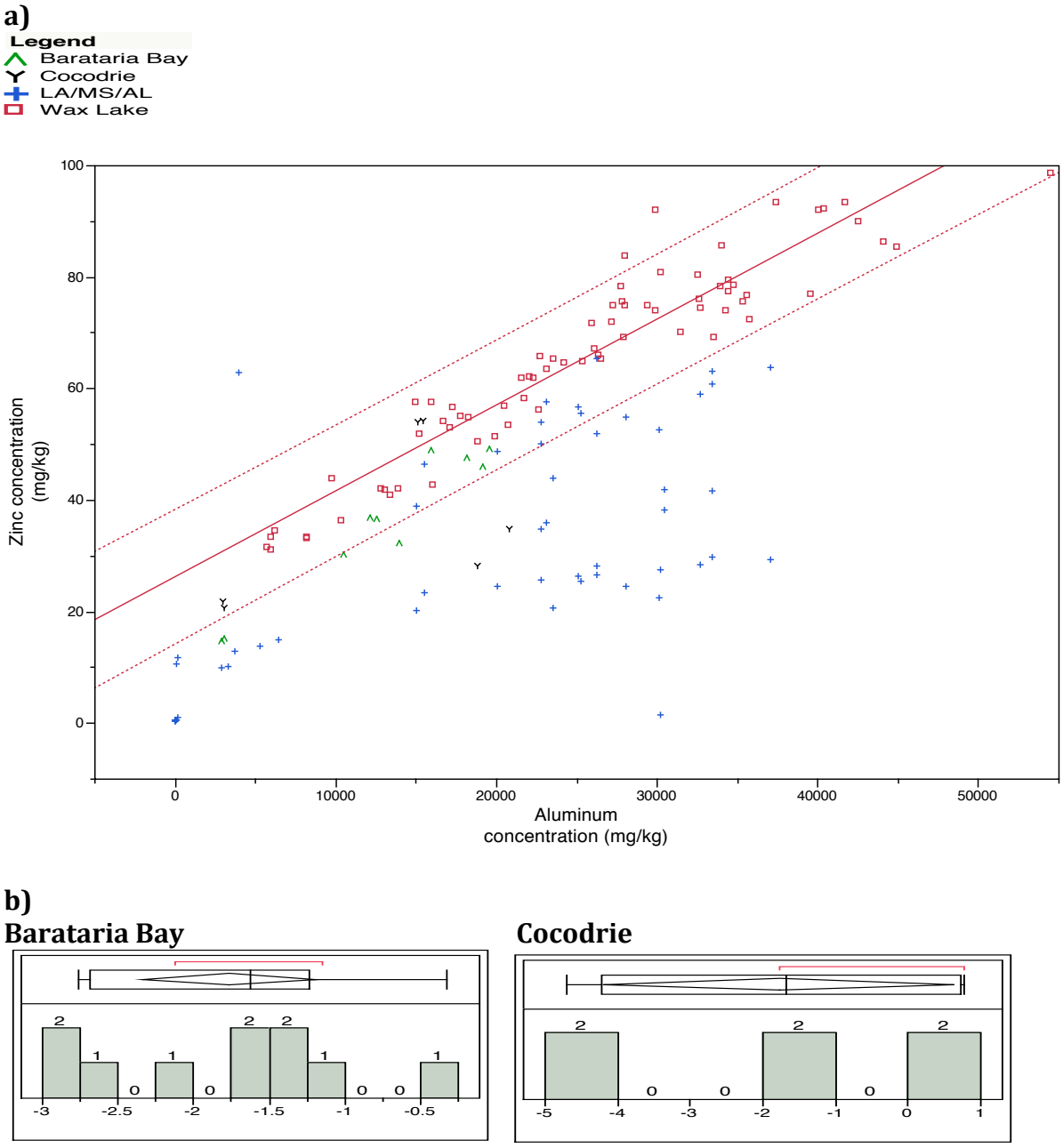


Figure 3.12 Zn vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Wax Lake as a Control Site

(Figure 3.12 continued)

Louisiana/Mississippi/Alabama **Wax Lake**

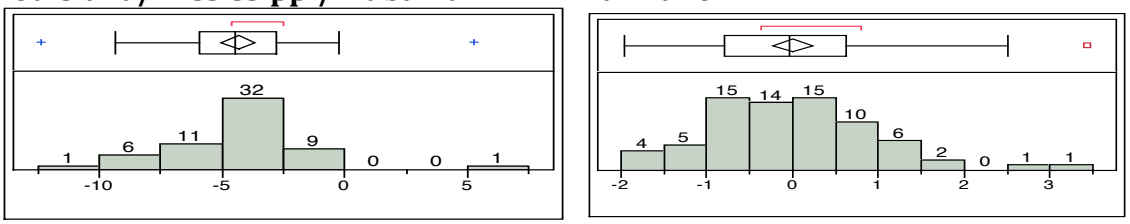


Table 3.9: Zn vs Al ANOVA for Sites in the Gulf of Mexico Region Using Wax Lake as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	84407	21102	181.15	<.0001
Error	144	16774	116.48940		
Corrected Total	148	101181			

Root MSE	10.79303	**R-Square**	0.8342
Dependent Mean	46.84900	**Adj R-Sq**	0.8296
Coeff Var	23.03790		

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Wax Lake	**1**	30.60059	2.35516	12.99	<.0001
AlumConc	**1**	0.00136	0.00007838	17.41	<.0001
LAMSAL	**1**	-26.53841	1.98713	-13.36	<.0001
BaraBay	**1**	-12.42625	3.76957	-3.30	0.0012
Cocodrie	**1**	-12.47429	4.68939	-2.66	0.0087

The significance in the ANOVA table may not be due elevated levels of Zn, but due to the fact that these concentrations are well below the linear regression line creating a false positive. These results support that there was no zinc elevation in any of the suspect sites.

3.3.4.2 Zn/Al Comparison to Pre-spill GoM as a Control

Figure 3.13 and Table 3.10 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the Zn/Al ratios of the sample test sites using pre-spill GoM sediment samples as a control. LA/MS/AL, Barataria Bay, and Cocodrie sites are all shown to be below the lower confidence limit pre-spill GoM (Figure 3.13a). None of these sites scored over -1 on the Approximated Studentized values (Figure 3.13b). The parameter estimate for pre-spill GoM is 38.12 and is statistically significant. No site was found to be above the pre-spill GoM parameter estimate (Table 3.10). These results show that none of these suspect sites had zinc elevation.

a)

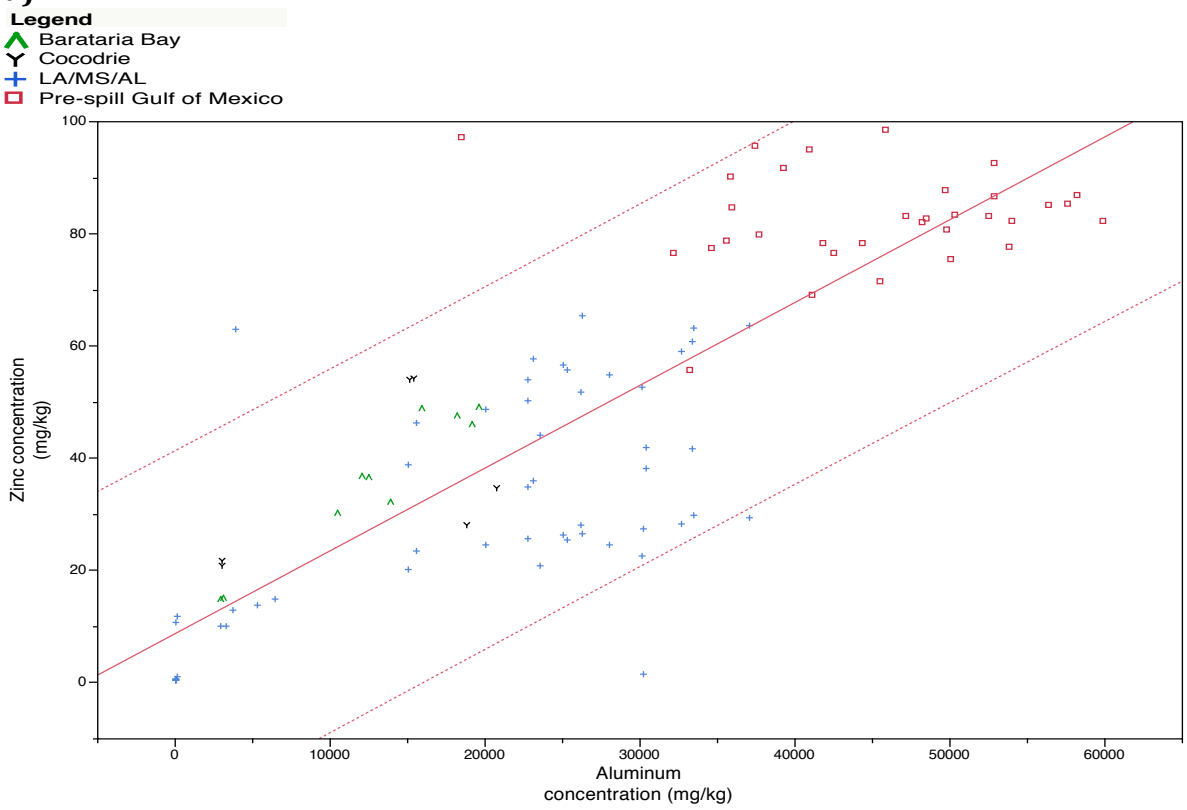
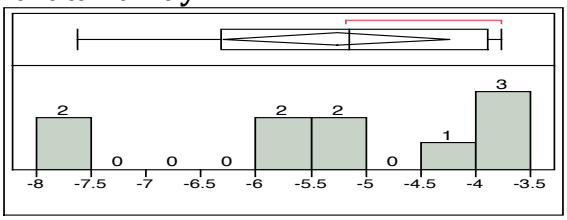


Figure 3.13 Zn vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site

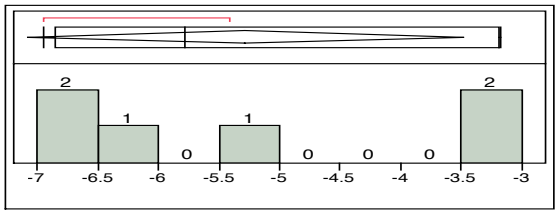
(Figure 3.13 continued)

b)

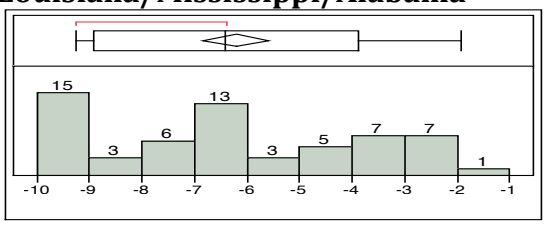
Barataria Bay



Cocodrie



Louisiana/Mississippi/Alabama



Pre-spill Gulf of Mexico

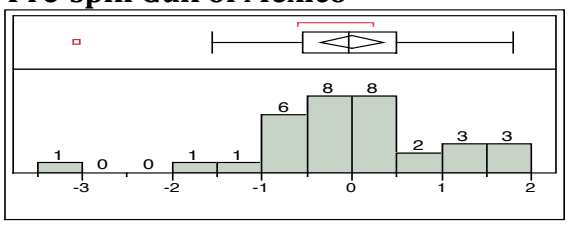


Table 3.10: Zn vs Al ANOVA for Sites in the Gulf of Mexico Region Using Pre-spill GoM as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	80092	20023	107.03	<.0001
Error	104	19456	187.07607		
Corrected Total	108	99548			

Root MSE	13.67758	**R-Square**	0.8046
Dependent Mean	45.41972	**Adj R-Sq**	0.7970
Coeff Var	30.11373		

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Pre-spill GoM	**1**	38.12224	5.80377	6.57	<.0001
AlumConc	**1**	0.00099165	0.00011761	8.43	<.0001
LAMSAL	**1**	-27.65269	4.41570	-6.26	<.0001
BaraBay	**1**	-15.16217	6.22076	-2.44	0.0165
Cocodrie	**1**	-15.24779	7.15922	-2.13	0.0355

3.3.4.3 Zn/Fe Comparison to Wax Lake as a Control

Figure 3.14 and Table 3.11 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the Zn/Fe ratios of the sample test sites using Wax Lake sediment samples as a control. Some points from LA/MS/AL and Cocodrie were outside the confidence limits of Wax Lake (Figure 3.14a). LA/MS/AL and Cocodrie had a few points that scored about 2.5 on the Approximated Studentized values, however Barataria Bay did not score above 0.5 (Figure 3.14b).

a)

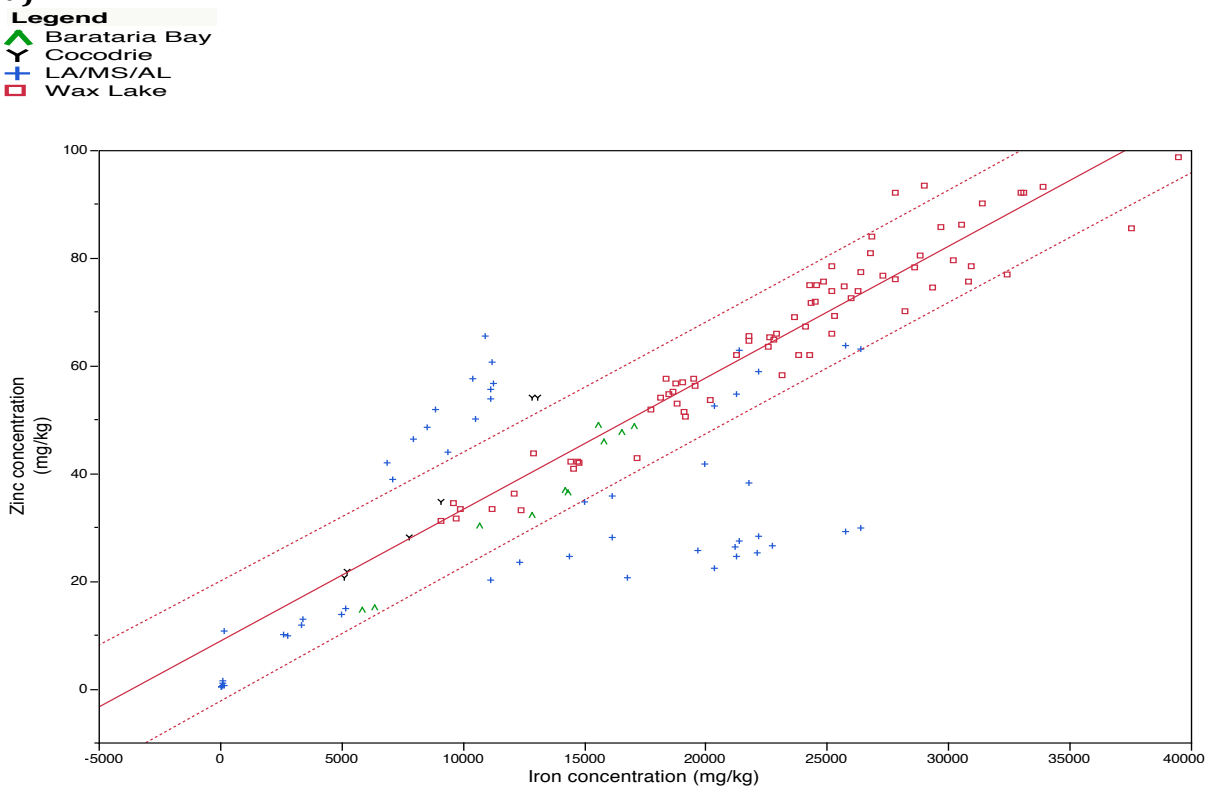
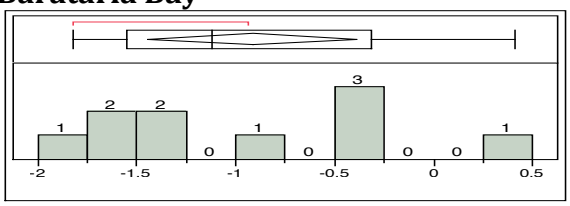


Figure 3.14 Zn vs Fe for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Wax Lake as a Control Site

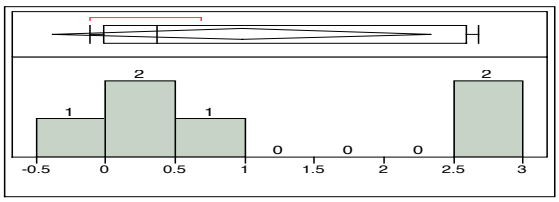
(Figure3.14 continued)

b)

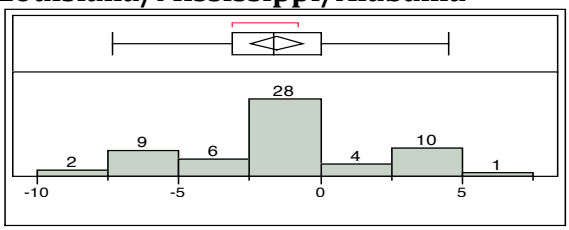
Barataria Bay



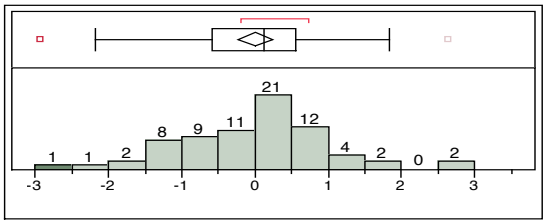
Cocodrie



Louisiana/Mississippi/Alabama



Wax Lake



The parameter estimate for Wax Lake is 19.97 and is statistically significant. LA/MS/AL and Barataria Bay are statistically significant, but only because with one exception where a Zn/Fe value is barely above the Wax Lake regression line, all the other Barataria Bay samples are below this line. Cocodrie is statistically insignificant (Table 3.11).

Table 3.11: Zn vs Fe ANOVA for Samples from Gulf of Mexico Using Wax Lake as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	81077	20269	145.18	<.0001
Error	144	20104	139.61444		
Corrected Total	148	101181			

Root MSE	11.81586	**R-Square**	0.8013
Dependent Mean	46.84900	**Adj R-Sq**	0.7958
Coeff Var	25.22115		

(Table 3.11 continued)

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Wax Lake	**1**	19.97057	3.29326	6.06	<.0001
IronConc	**1**	0.00196	0.00012943	15.14	<.0001
LAMSAL	**1**	-13.81928	2.59423	-5.33	<.0001
BaraBay	**1**	-9.64852	4.19516	-2.30	0.0229
Cocodrie	**1**	-1.84526	5.34511	-0.35	0.7304

3.3.4.4 Zn/Fe Comparison to pre-spill GoM as a Control

Figure 3.15 and Table 3.12 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the Zn/Fe ratios of the sample test sites using pre-spill GoM sediment samples as a control. LA/MS/AL, Barataria Bay, and Cocodrie were all under or with the confidence limits of pre-spill GoM (Figure 3.15a). None of these sites scored above a -1.0 on the Approximated Studentized values histogram (Figure 3.15b). In the ANOVA table, the parameter estimate for pre-spill GoM is 29.79 and is statistically significant. LA/MS/AL is statistically significant, but did not have a parameter estimate that exceeded pre-spill GoM. Barataria Bay and Cocodrie are statistically insignificant (Table 3.12). These results support that there is no elevation in zinc for suspect sites using GoM samples as the control site.

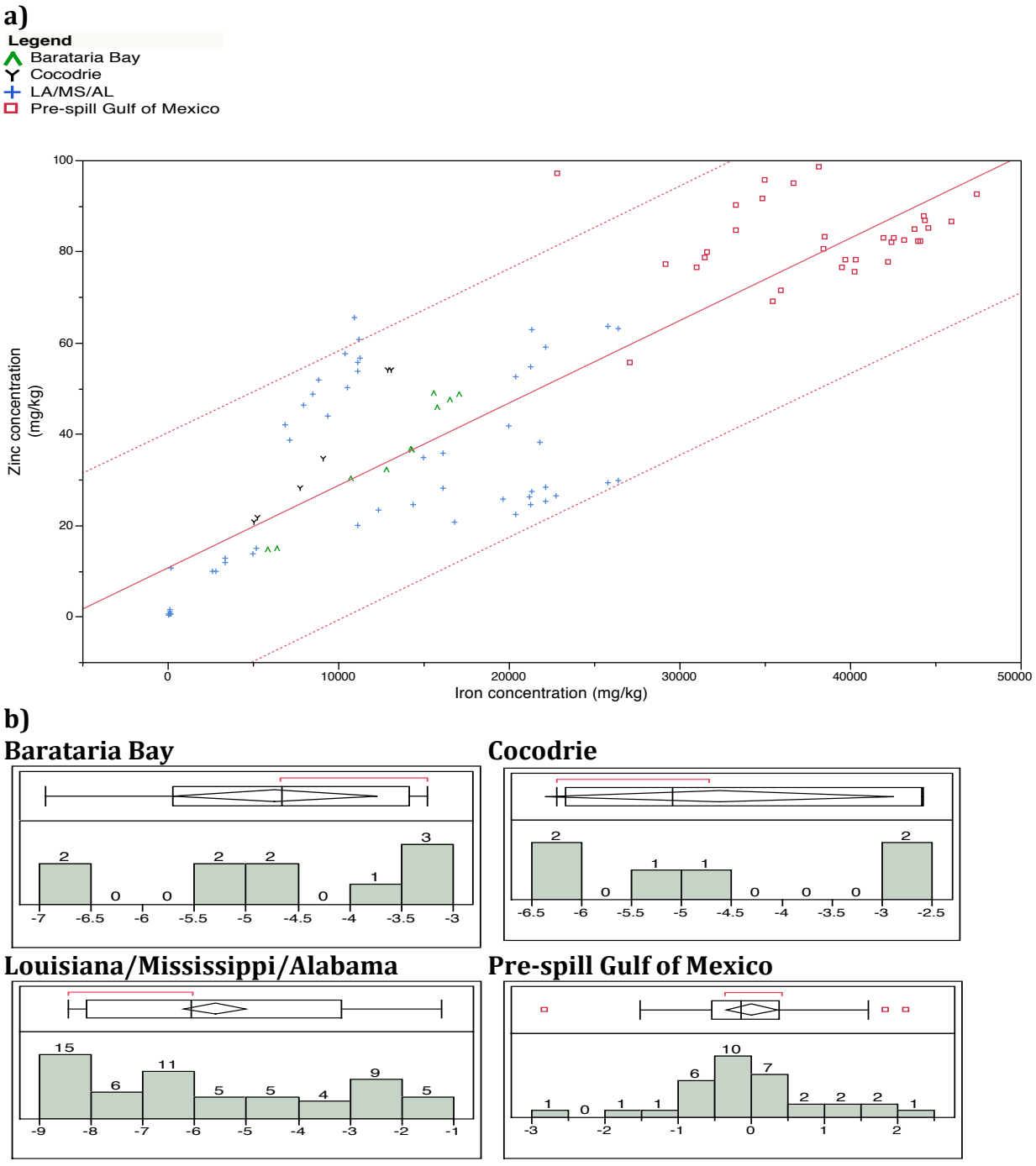


Figure 3.15 Zn vs Fe in Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site

Table 3.12: Zn vs Fe ANOVA for Sites in the Gulf of Mexico Using Pre-spill GoM as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	78547	19637	97.24	<.0001
Error	104	21001	201.93501		
Corrected Total	108	99548			

Root MSE	14.21038	**R-Square**	0.7890
Dependent Mean	45.41972	**Adj R-Sq**	0.7809
Coeff Var	31.28681		

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Pre-spill GoM	**1**	29.79053	7.36898	4.04	0.0001
IronConc	**1**	0.00138	0.00018125	7.63	<.0001
LAMSAL	**1**	-17.35972	5.84345	-2.97	0.0037
BaraBay	**1**	-12.00952	6.88700	-1.74	0.0841
Cocodrie	**1**	-6.55582	8.25982	-0.79	0.4292

Almost all points from sites LA/MS/AL, Barataria Bay, and Cocodrie are within or below the confidence limits of figures 3.12a, 3.13a, 3.14a, and 3.15a. The Approximated Studentized values in figures 3.12b, 3.13b, 3.14b, and 3.15b all show, with the exception of one sample for Cocodrie and one sample for LA/MS/AL in Figure 3.14b, that the sites in question were below a critical score of 2.5. These scores are to be expected, as zinc is not typically found an elevated concentration in crude oil and as mentioned previously, Zn was included in this study as a method

evaluation test because no Zn contamination is expected for any of these sites. The test results in Tables 3.9, 3.10, 3.11, and 3.12 further support that these results are significant because they are below the Pr > |t| value of 0.05, save for Cocodrie in Tables 3.11 and 3.12 and Barataria Bay in Table 3.12 as these sites exceed the Pr > |t| limit of 0.05. These samples that are significant may not be elevated in Zn/Al and Zn/Fe concentrations.

3.3.5 Magnesium Evaluation in Areas Known to Have Contaminated Sites

3.3.5.1 Mg/Al Comparison to Wax Lake as a Control

Figure 3.16 and Table 3.13 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the Mg/Al ratios of the sample test sites using Wax Lake sediment samples as a control. A very few points from LA/MS/AL are above the upper confidence limit of Wax Lake. Barataria Bay and Cocodrie are shown as within or below the confidence limits of Wax Lake (Figure 3.16a). LA/MS/AL, Barataria Bay, nor Cocodrie scored above 2.5 on the Approximated Studentized values (Figure 3.16b). The parameter estimate (useful for baseline comparison) for Wax Lake is statistically significant with a value of 3442.2. LA/MS/AL, Barataria Bay, and Cocodrie are all statistically significant, but because of low Mg/Al ratios, not elevated ratios (Table 3.13). These results support that the suspect sites have no elevated concentration of magnesium.

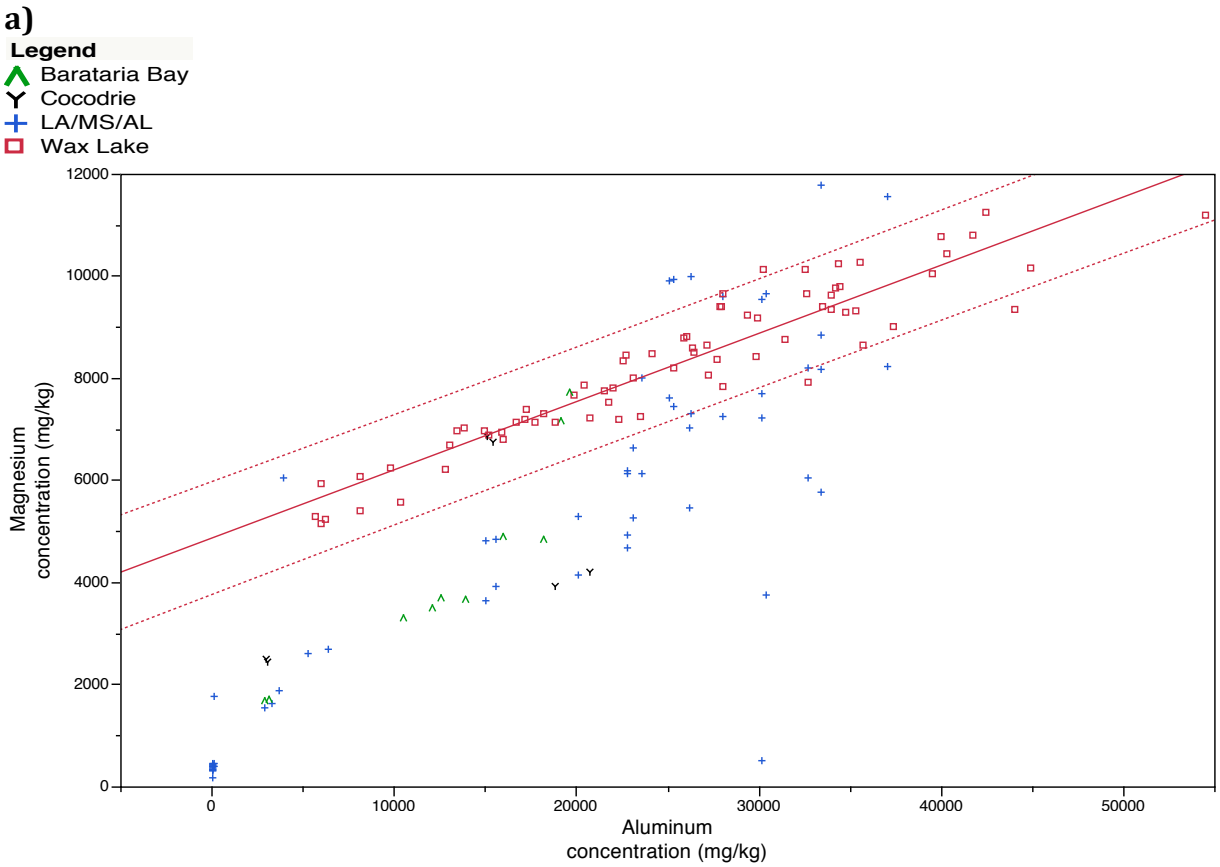


Figure 3.16 Mg vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Wax Lake as a Control Site

Table 3.13: Mg vs Al ANOVA for Gulf of Mexico samples using Wax Lake as a control site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	1160068054	290017013	156.16	<.0001
Error	144	267425782	1857123		
Corrected Total	148	1427493836			

Root MSE	1362.76318	**R-Square**	0.8127
Dependent Mean	6427.50867	**Adj R-Sq**	0.8075
Coeff Var	21.20204		

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Wax Lake	**1**	3442.29087	297.36999	11.58	<.0001
AlumConc	**1**	0.18959	0.00990	19.16	<.0001
LAMSAL	**1**	-1921.63386	250.90166	-7.66	<.0001
BaraBay	**1**	-1658.44782	475.95869	-3.48	0.0007
Cocodrie	**1**	-1413.53743	592.09776	-2.39	0.0183

3.3.5.2 Mg/Al Comparison to Pre-spill GoM as a Control

Figure 3.17 and Table 3.14 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the Mg/Al ratios of the sample test sites using pre-spill GoM sediment samples as a control. LA/MS/AL, Barataria Bay, and Cocodrie were all found to be within or below the confidence limits of pre-spill GoM (3.17a). None of these sites scored higher than 2.0 on the Approximated Studentized values (Figure 3.17b). Pre-spill

GoM has a parameter estimate of 5297.0 and is statistically significant. LA/MS/AL, Barataria Bay, and Cocodrie are all statistically significant, but all have parameter estimates less than pre-spill GoM (Table 3.14). Magnesium, as well as Zn, was selected in this supplemental tracking methods evaluation because Mg contamination is not an issue with any of these sites and a contamination event would not show up in sediments because of the high solubility of Mg and high Mg in seawater.

a)

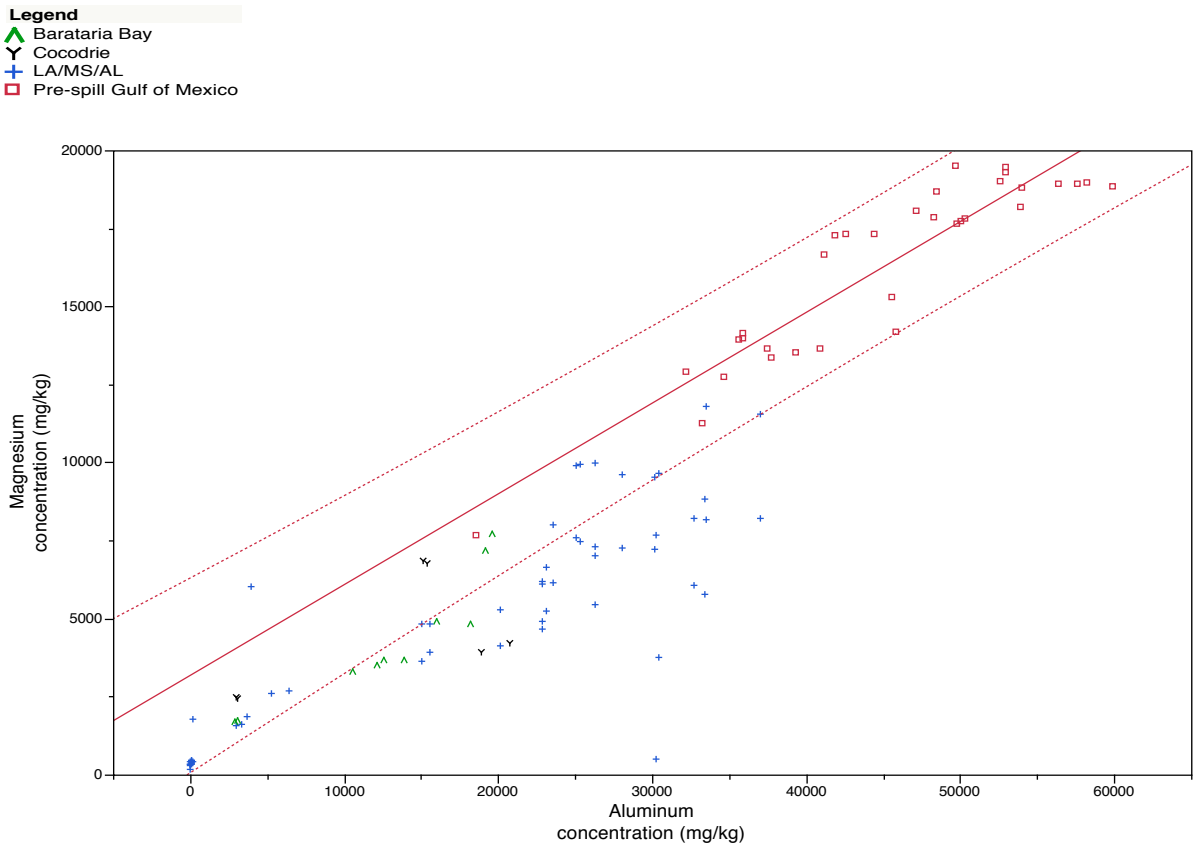
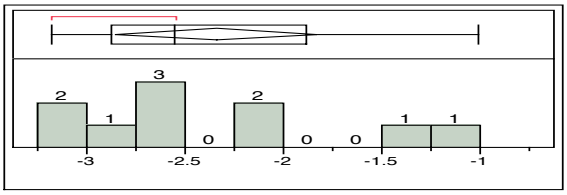


Figure 3.17 Mg vs Al for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site

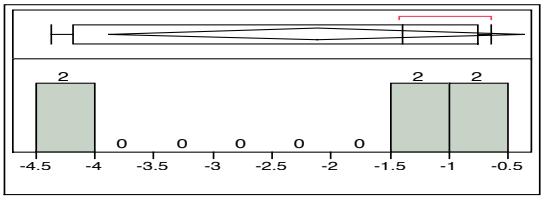
(Figure 3.17 continued)

b)

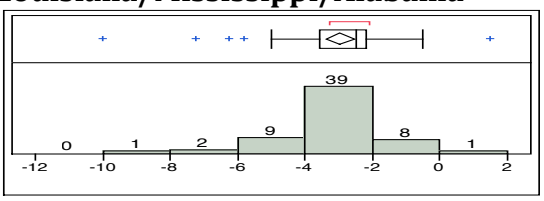
Barataria Bay



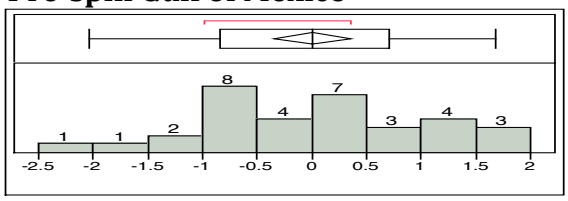
Cocodrie



Louisiana/Mississippi/Alabama



Pre-spill Gulf of Mexico



If the data shows any significance it is due to Mg being very high in seawater and the Barataria Bay, Cocodrie, and LA/MS/AL sites all have less salinity (thus less Mg) than open sea water such as found in the Gulf of Mexico. These results support that there is no elevated concentration of magnesium in these suspect sites.

Table 3.14 Mg vs Al ANOVA for Gulf of Mexico Samples Using Pre-spill GoM as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	3891955464	972988866	402.99	<.0001
Error	104	251100959	2414432		
Corrected Total	108	4143056423			

Root MSE	1553.84436	**R-Square**	0.9394
Dependent Mean	8183.25321	**Adj R-Sq**	0.9371
Coeff Var	18.98810		

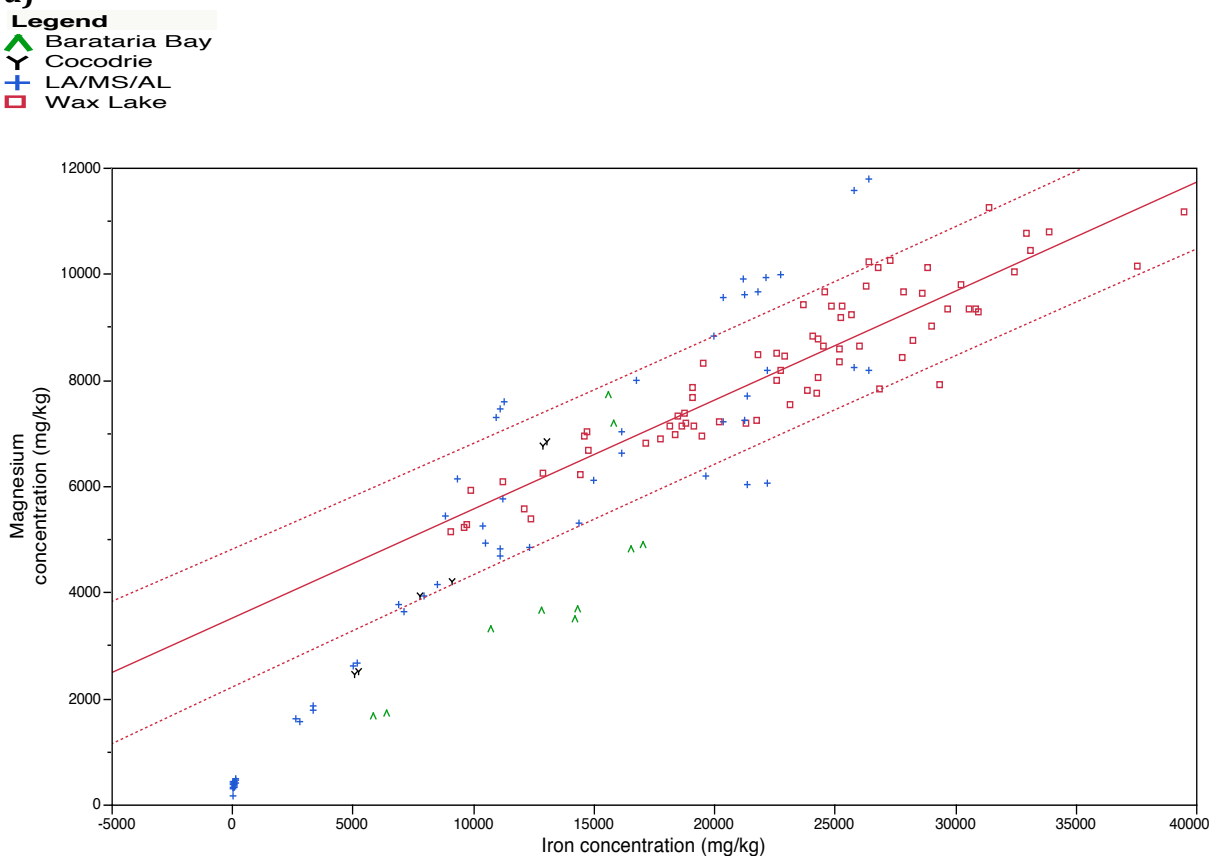
(Table 3.14 continued)

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Pre-spill GoM	**1**	5297.03195	659.33828	8.03	<.0001
AlumConc	**1**	0.24357	0.01336	18.23	<.0001
LAMSAL	**1**	-4703.55894	501.64643	-9.38	<.0001
BaraBay	**1**	-4205.56591	706.71130	-5.95	<.0001
Cocodrie	**1**	-3955.58645	813.32522	-4.86	<.0001

3.3.5.3 Mg/Fe Comparison to Wax Lake as a Control

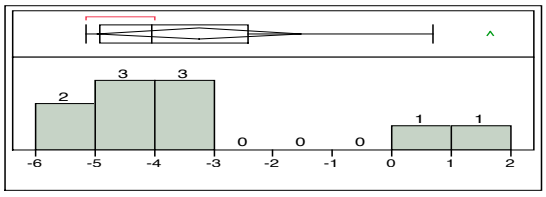
Figure 3.18 and Table 3.15 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the Mg/Fe ratios of the sample test sites using Wax Lake sediment samples as a control. LA/MS/AL has a few points outside the upper confidence limits of Wax Lake, (primarily because most LA/MS/AL samples were GoM beach sites and some evaporation of seawater may have occurred increasing Mg levels, and the Wax Lake waters have lower salinities) while Barataria Bay and Cocodrie have all points within or below the Wax Lake confidence limits (Figure 3.18a). Only a few data points from LA/MS/AL scored higher than 2.5 in the Approximated Studentized values, again a function of indigenous salinity and possibly some evaporation on the beach rather than contamination (Figure 3.18b). Wax Lake has a parameter estimate of 1200.8 and is statistically significant. Barataria Bay has a parameter of -936.46 and is statically significant, but due to samples being below the GoM regression line LA/MS/AL and Cocodrie were not exhibiting elevated Mg (Table 3.15).

a)

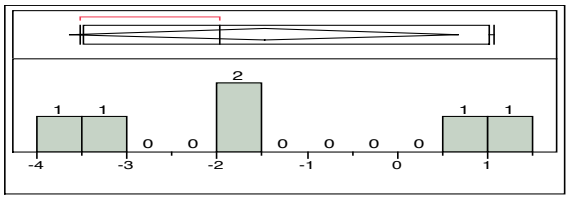


b)

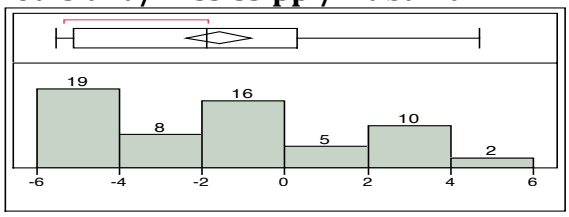
Barataria Bay



Cocodrie



Louisiana/Mississippi/Alabama



Wax Lake

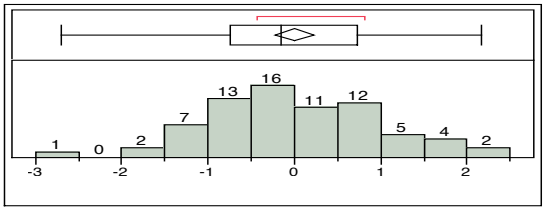


Figure 3.18 Mg vs Fe for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Wax Lake as a Control Site

Table 3.15 Mg vs Fe ANOVA for Gulf of Mexico Region Using Wax Lake as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	1255191139	313797785	262.25	<.0001
Error	144	172302697	1196547		
Corrected Total	148	1427493836			

Root MSE	1093.86768	**R-Square**	0.8793
Dependent Mean	6427.50867	**Adj R-Sq**	0.8759
Coeff Var	17.01853		

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Wax Lake	**1**	1200.84051	304.87752	3.94	0.0001
IronConc	**1**	0.30528	0.01198	25.48	<.0001
LAMSAL	**1**	249.05137	240.16404	1.04	0.3015
BaraBay	**1**	-936.46820	388.37189	-2.41	0.0172
Cocodrie	**1**	534.01577	494.83031	1.08	0.2823

3.3.5.4 Mg/Fe Comparison to Pre-spill GoM as a Control

Figure 3.19 and Table 3.16 presents the simple linear regression, Approximated Studentized values, and ANOVA statistical figures and tables for the Mg/Fe ratios of the sample test sites using pre-spill GoM sediment samples as a control. LA/MS/AL has multiple points that are outside the upper confidence limits of pre-spill GoM where some seawater evaporation on a beach may be a factor, however Barataria Bay and Cocodrie were within or below the confidence limits of

pre-spill GoM (Figure 3.19a). LA/MS/AL and Cocodrie test sites have at least one point that scored past 2.5 in the Approximated Studentized values histogram, Barataria Bay did not score past 2.5 (Figure 3.19b). Pre-spill GoM has a parameter estimate of 1365.8 and is statistically significant. Barataria Bay is the only statistically significant site with a parameter estimate of -2183.4 (Table 3.16). These results support there is no elevated magnesium concentration at suspect sites as was anticipated.

a)

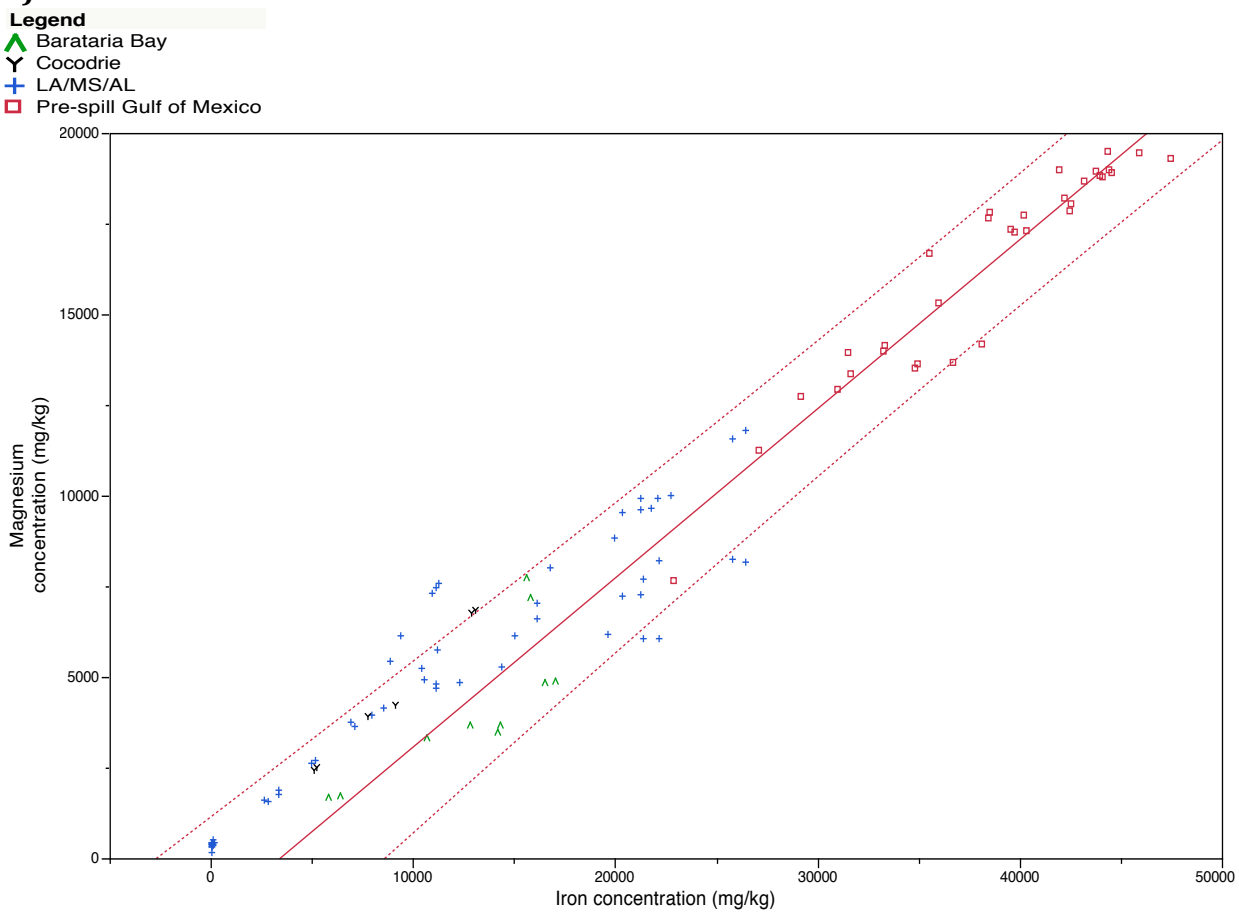
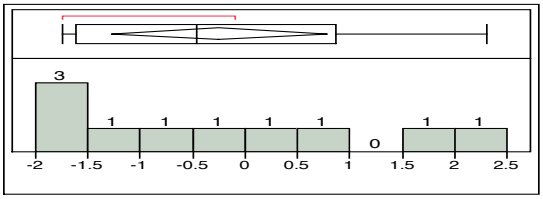


Figure 3.19 Mg vs Fe for Sites in the Gulf of Mexico Region with Approximated Studentized Values Using Pre-spill GoM as a Control Site

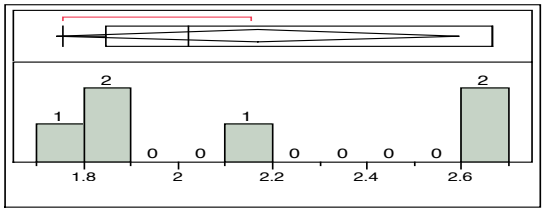
(Figure 3.19 continued)

b)

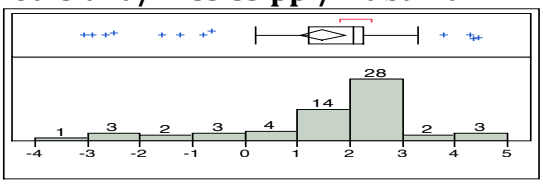
Barataria Bay



Cocodrie



Louisiana/Mississippi/Alabama



Pre-spill Gulf of Mexico

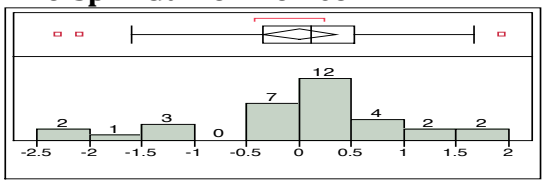


Table 3.16 Mg vs Fe ANOVA for Gulf of Mexico Samples Using Pre-spill GoM as a Control Site

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	4019128655	1004782164	843.21	<.0001
Error	104	123927768	1191613		
Corrected Total	108	4143056423			

Root MSE	1091.61035	**R-Square**	0.9701
Dependent Mean	8183.25321	**Adj R-Sq**	0.9689
Coeff Var	13.33956		

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Pre-spill GoM	**1**	1365.80182	566.06906	2.41	0.0176
IronConc	**1**	0.38888	0.01392	27.93	<.0001
LAMSAL	**1**	-826.99264	448.88088	-1.84	0.0683
BaraBay	**1**	-2183.40788	529.04382	-4.13	<.0001
Cocodrie	**1**	-372.37695	634.50127	-0.59	0.5586

Almost all points from sites LA/MS/AL, Barataria Bay, and Cocodrie are within or below the confidence limits of Figures 3.16a, 3.17a, 3.18a, and 3.19a. The Approximated Studentized values in Figures 3.16b, 3.17b, 3.18b, and 3.19b all show, except for two instances of LA/MS/AL and one instance of Cocodrie for Figures 3.18b and 3.19b, that the sites in question were below a critical score of 2.5 and some of these events were due to high Mg in seawater and expected salinity differences between the sites and some possible concentration by seawater evaporation from exposed beach sites in the LA/MS/AL data sets. The test results in Tables 3.13, 3.14, 3.15, and 3.16 further support that these results are significant, save for LA/MS/AL and Cocodrie in Figures 3.16 and 3.17, and are not elevated in Mg/Al and Mg/Fe ratios after considering salinity differences between sites.

3.4 Vanadium and Nickel versus Calcium and Magnesium in Water

Originally it was intended to collect clean coastal water for control samples and water contaminated with the Deepwater Horizon oil spill to varying degrees – from water visibly clean near spill impacted water to water visibly containing crude oil over hopefully a wide geographical area. However, we were unable to obtain the water samples we needed for a thorough study of using V and Ni as a supplemental tracking method for oil spills in the ocean and coastal water. The proposal for this work, to keep the budget low, included the premise that we would be able to obtain appropriate water samples from others funded for ship time sampling over a wide area in the Gulf of Mexico, including water visibly containing oil. However, some researchers known to us and generally wanting to cooperate with our efforts were not allowed by their funding sources to pass on samples believed to be impacted to

other investigations. Some samples that may have been influenced by the spill, to a small degree, were obtained.

Regarding water analyses and evaluation, our focus thus shifted more to a brief, preliminary evaluation of V and Ni ratios with calcium (Ca) and magnesium (Mg) in water serving as the abundant "normalization" metals. Both Ca and Mg are very soluble in addition to being abundant in seawater whereas, Al and Fe, while being abundant in soils and sediments, are very sparingly soluble in water. In water, V/Fe, Ni/Fe, V/Al, and Ni/Al ratios did not provide a clear linear regression because Fe and Al are sparingly soluble in oxidized, near neutral pH water. We decided to include the water data obtained mostly from non-oil-impacted coastal bay and Gulf of Mexico sources as a background data set for V and Ni in coastal waters since very little work has been done reporting especially V in water samples. While a few of our water samples may have been influenced by the oil spill, we just did not have sufficient documentation most of these were truly spill-impacted samples. Unlike trace metal impacted soils and sediments where the metals bind and remain with the solid phase for extended periods, trace levels of metals in surface waters are subject to major dilution and transport effects in coastal and ocean waters in complex current systems. For possible oil spills occurring in the future from oil sources containing elevated levels of V and Ni, making these water data available may be useful to other researchers in the future interested in background levels of V and Ni in coastal waters. V and Ni to Ca and Mg ratios did not produce adequate linear regressions or significant data results, thus the decision to just include the concentration data as an appendix table (Appendix A).

3.5 Overall Implications for Sediment Data and Analysis

3.5.1 Likely Concentration of Vanadium and Nickel in Weathered Macondo Crude Oil

The MC252 prospect wellhead had relatively low values of V and Ni in its crude oil, but obviously oiled sediment samples in our work tended to be substantially elevated in V and Ni compared to baseline sediment. There may be several reasons behind this apparent discrepancy. The constituents found in crude oil can undergo concentration changes depending on the weathering (Liu et al., 2012). Crude oil passing through seawater is capable of absorbing some metal ions and increasing concentration of heavier crude oil constituents while losing other lower molecular weight constituents (Liu et al., 2012; Joung and Shiller, 2013). Studies have shown that V and Ni concentrations increase if crude oil is exposed to increased weathering (Liu et al., 2012). As the lower molecular weight petroleum compounds separate from the bulk of the spilled oil by volatilization at the water surface, or separation from heavier weight petroleum compounds in the water by solubility and density differences, the heavier weight residual petroleum compounds containing V and Ni subsequently contain higher metal concentrations than the original spilled crude oil. Degradation of the lower molecular weight compounds can also be more rapid than the larger molecular weight fraction (Liu et al., 2012) contributing to a metal concentration effect.

3.5.2 Analysis of V and Ni Concentration Ratios with Fe and Al

Three different statistical analyses were utilized in the analyses of these data (see Section 2.4). Each statistical output had various uses and explanations behind what the analyses meant and was presented earlier in this chapter.

Simple linear regression was presented first for each comparison and was important to give a visual representation of how each data point compared to one another and visually expressed if data points were outside a defined confidence interval, thus indicating possible elevation in concentration. This technique was important to display how different, numerically, a possibly contaminated concentration of an element of interest : conservative element ratio was to uncontaminated samples.

The Approximated Studentized values analysis is able to point out a key difference in scores where elevated concentrations or ratios may exist in a data set based on a critical comparison score. This system was useful visually, showing the amount of data for each score based on a percentage of the data found to be elevated in concentration or ratios by this statistical evaluation technique.

The multiple linear regression analysis and ANOVA table is a statistical method that is able to compare multiple linear regressions, a t-score, a parameter estimate, and indicate statistical significance or insignificance. This method is superior in a multitude of ways, however, the statistic that was important in this method was the parameter estimate as it provided a new statistical analysis to support if an area was different in concentration when compared to a control site. Thus three statistical procedures were compared to evaluate methods of possibly identifying where a trace element being used as a spill tracking tool or a spill-impacted site might be useful in identifying impacted sediment areas. There was frequent support among the three different statistical tools in identifying possible contaminated sites. The multiple linear regression technique frequently showed

significant differences that were not indicative of elevated V and Ni levels due to some V and Ni points being not elevated, but instead lower than typical ratios or normal ratios as was clearly evident looking at the regression plots.

ANOVA is an excellent tool to compare multiple means and multivariate analysis. However, ANOVA cannot provide information on where the difference is located between these means and multivariate analyses. Alternative methods allow for post-tests that can delve into the realm of why means are different and possibly indicate false positive ANOVA tests.

Approximated Studentized values are not as powerful a statistical tool compared to the ANOVA test, but when an ANOVA test indicates that means are significantly different it is viable to use a posttest. In Table 3.18, it is apparent that there are false positives in the ANOVA test. Put simply, there are instances where the Approximated Studentized values do not match up with ANOVA results. Table 3.18 also depicts Z-score results with the ANOVA significance results. This result is most noticeable in the pre-spill GoM sites, for example, the V/Al ratio for LA/MS/AL for all three tests is significant, but the V/Al ratio for Barataria Bay is insignificant for the simple linear regression and Approximated Studentized values but significant for the ANOVA. The reasoning behind this test showing a false positive may be due to consistently low elemental ratios. The ANOVA is consistently showing significance in these sites, when in reality; there is not a significance of these sites, Barataria Bay and Cocodrie, being elevated in element ratios. Considering this, the three statistical methods evaluated showed reasonably good agreement.

Table 3.19 explains the parallelogram over the z-scoring method found in the Approximated Studentized values figures. Each area as its midpoint line, think of this similar to the median of the parallelogram, and the z-score summary of the parallelogram, think of this as the adjusted mean of the parallelogram. The z-score summary parallelogram is the variable used in determining if the z-score is statistically significant as it incorporates all of the listed points in the figure and summarizes those points into an adjusted mean score. This adjusted mean is then used to support if the area in question is indeed elevated in concentration for overall data. However, if there were any points that scored over the critical score of 2.5 in the Approximated Studentized values z-score, then elevation of the element in the area can be supported by this test. With this is mind, looking at table 3.19 shows that most of these areas may not be elevated in concentration, but this table is only showing the test scores for the parallelogram mean and median, it does not reflect on all known scores. The reasoning behind presenting this table is to compare all statistical results, including results that do not represent apparent elevation, and explain that a median z-score and mean z-score of the parallelogram are not solely indicative of elevation or no elevation of the element in the area.

Table 3.18 Comparison of the Three Statistical Methods in Indicating Elevated Sediment V or Ni

Elemental Comparison	Visual evaluation of regression points	Any points past z-score critical value	Statistically Significant ANOVA
Gulf of Mexico Baseline			
V/Al			
LA/MS/AL	Yes, many points	Yes	Yes
Barataria Bay	No	No	Yes
Cocodrie	No	No	Yes
V/Fe			
LA/MS/AL	Yes, many points	Yes	Yes
Barataria Bay	No	No	Yes
Cocodrie	No	No	Yes
Ni/Al			
LA/MS/AL	Yes, many points	Yes	Yes
Barataria Bay	No	No	Yes
Cocodrie	No	No	Yes
Ni/Fe			
LA/MS/AL	Yes, many points	Yes	Yes
Barataria Bay	No	No	Yes
Cocodrie	No	No	Yes
Wax Lake Baseline			
V/Al			
LA/MS/AL	Yes, many points	Yes	Yes
Barataria Bay	No	No	No
Cocodrie	No	No	No
V/Fe			
LA/MS/AL	Yes, many points	Yes	Yes
Barataria Bay	No	No	No
Cocodrie	Yes, one point	Yes	Yes
Ni/Al			
LA/MS/AL	Yes	Yes	Yes
Barataria Bay	No	No	No
Cocodrie	No	No	No
Ni/Fe			
LA/MS/AL	Yes, many points	Yes	Yes
Barataria Bay	Yes, few points	No	Yes
Cocodrie	Yes, many points	Yes	Yes

Table 3.19 Summary of Mean and Median Z-Scores of Approximated Studentized Values

Elemental Comparison	Z-score summary midpoint/median (short line in center of parallelogram)	Z-score Parallelogram summary/mean
Gulf of Mexico Baseline		
V/Al		
LA/MS/AL	0.5	0.5
Barataria Bay	-2.2	-2
Cocodrie	-1.6	-1.6
V/Fe		
LA/MS/AL	0.8	-0.4
Barataria Bay	-2.3	-2
Cocodrie	-1.2	-1.5
Ni/Al		
LA/MS/AL	-2	7
Barataria Bay	-3	-2.8
Cocodrie	-2.6	-2.6
Ni/Fe		
LA/MS/AL	0	8
Barataria Bay	-3.5	-2.2
Cocodrie	-1.2	-1.6
Wax Lake Baseline		
V/Al		
LA/MS/AL	1	1
Barataria Bay	-1.2	-1
Cocodrie	-0.7	-0.5
V/Fe		
LA/MS/AL	3	3
Barataria Bay	-1	0
Cocodrie	1.6	1.6
Ni/Al		
LA/MS/AL	0	10
Barataria Bay	-0.6	-0.5
Cocodrie	-0.4	-0.4
Ni/Fe		
LA/MS/AL	3	15
Barataria Bay	0	0.4
Cocodrie	2.6	2.3

The purpose of the graphs and tables for the trace element / conservative element ratios in this work was to further delve into the possibility that oil spill impacts on sediments can be found using vanadium or nickel as a component in a ratio with a conservative element, such as V/Fe, Ni/Al, etc., in a coastal sediment system. By providing visual and statistical analyses in Figures 3.4 – 3.11 and Tables 3.1 – 3.8 there is evidence that oil-impacted sediments can be identified by using this method. Zinc and Mg were included in the sediment phase of this study because it was thought that they should not show elevated levels with oil impacted sediment as V and Ni might, and this hypothesis turned out to be true.

3.6 Conclusion

Though the Deepwater Horizon crude oil spill contained relatively low levels of V and Ni, literature sources were presented explaining how weathering and other processes affecting crude oil spills can result in an increase in trace metal content of residual crude oil. We focused on identifying contaminated sediments with ratios of V and Ni versus the conservative elements Al and Fe found in abundance in silt-like and clayey sediments. These ratios compensated for the fact that all metals, both elements of primary interest and conservative elements tend to be correlated with clay content of sediments, thus a straight concentration determination is not useful as sediments in different locations vary widely in sand, silt, and clay content.

Simple linear regression, Approximated Studentized Values, and multiple linear regressions analysis or ANOVA were shown to be useful to determine if there is crude oil contamination of sediment in an area. Simple linear regression analyses with appropriate confidence limits on plots including ratios of samples in control

sites as well as possibly impacted sites gave a good visual and some statistical indication of contaminated sediments, which was useful in evaluating the results of other statistical techniques. The Approximated Studentized Values test appeared to be a good statistical tool to identify contaminated sediments. The multiple linear regression, ANOVA, statistical tool was also useful, but indicated false positive results for elevated Ni and V when some samples had lower than control site values. This situation was apparent when also looking at the results of the other two statistical tools.

While this work does not confirm this method could be uses as a complementary method to identify oil spill-impacted sediments, it represents an important step and useful preliminary information that looks very promising in developing a complimentary / supplemental method or screening method for tracking oil spills and identifying contaminated sediments that is less expensive and less time consuming than current methods using gas chromatography / mass spectrometry analysis. It has already been reported that V/Ni ratios may be used to determine if crude oil is in an area (see Literature Review section 1.11.3). Thus it stands to reason that this method could be viable with further research.

This work has established that extractable levels of V and Ni versus Al and Fe ratios may be useful top determine crude oil contamination in an areas as has been successfully done with other metals-contaminated sites (DeLaune et al., 2008). There are other elements also found in crude oil that might be useful in a similar effort that this work supports, such as cobalt and copper (Table 1.1). The conclusion is this work provides useful preliminary information on a supplemental

crude oil tracking / impact area identification, and raises several questions and possible discussions for future research.

It is highly possible to develop a complementary method to tracking crude oil in coastal systems. The questions that need to be asked to improve this method are, and questions that this research explored include: 1) which elements will produce consistent results identifying crude oil contamination in an area, 2) what are the appropriate statistical tools to use in such an effort, and, 3) how similar to the suspected contaminated sites must the control sites be for establishing baseline trace element / conservative element ratios in sediments. Providing more background information on elements found in crude oils and coastal environments will further progress in finding a faster and less expensive method to tracking crude oil spills and identifying contamination in an area that will compliment and supplement current methods more quickly and at less expense.

In summary, though additional work is necessary, the results of this work strongly indicate that extractable levels of V and Ni divided by levels of Al and Fe in the same sediments (V/Al, V/Fe, Ni/Al, and Ni/Fe ratios) may be useful in identifying crude oil-contaminated sediments. Though different crude oils vary greatly in V and Ni levels from very low to substantially elevated, weathering of spilled crude oil that increases V and Ni concentrations in residual crude oil may make this approach for identifying impacted sediments useful for some spills containing relatively low levels of these elements.

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APPENDIX

Table 3.17: V, Ni, Mg, and Ca in water samples from Gulf of Mexico using Brackish Louisiana bays A and J as a control site

Vanadium concentration (mg/kg)	Nickel concentration (mg/kg)	Magnesium concentration (mg/kg)	Calcium concentration (mg/kg)	Legend
0.010036	0.004852	20.1977	20.8999	Offshore Louisiana (non-algae)
0.008348	0.007189	29.4607	30.1577	Offshore Louisiana (non-algae)
0.007377	0.002325	30.0811	31.4456	Offshore Louisiana (non-algae)
0.000946	0.073864	42.742	15.3039	Offshore Louisiana (non-algae)
0.005515	0.007004	422.91	141.145	Offshore Louisiana (non-algae)
0.004816	0.004762	409.796	141.005	Offshore Louisiana (non-algae)
0.005598	0.006943	382.3	130.005	Offshore Louisiana (non-algae)
0.004301	0.005532	375.131	129.223	Offshore Louisiana (non-algae)
0.005913	0.009313	238.388	87.5452	Offshore Louisiana (non-algae)
0.003602	0.002005	221.99	83.608	Offshore Louisiana (non-algae)
0.00329	0.003619	246.425	91.3511	Offshore Louisiana (non-algae)
0.003177	0.005873	262.571	100.032	Offshore Louisiana (non-algae)
0.003222	0.009376	260.13	100.744	Offshore Louisiana (non-algae)
0.003442	0.005921	261.485	95.4775	Offshore Louisiana (non-algae)
0.00274	0.00748	290.696	104.28	Offshore Louisiana (non-algae)
0.002818	0.008367	276.597	100.904	Offshore Louisiana (non-algae)
0.004844	0.005816	188.824	71.2404	Offshore Louisiana (non-algae)
0.002358	0.004708	498.654	160.496	Offshore Louisiana (non-algae)
0.003039	0.008287	426.735	140.457	Offshore Louisiana (non-algae)
0.002569	0.006941	441.692	146.744	Offshore Louisiana (non-algae)
0.000871	0.004708	696.351	199.818	Offshore Louisiana (non-algae)
0.000304	0.006907	680.298	204.089	Offshore Louisiana (non-algae)
0.001552	0.004816	721.51	211.427	Offshore Louisiana (non-algae)
0.000527	0.003854	705.766	206.59	Offshore Louisiana (non-algae)
0.004222	0.007898	718.784	219.227	Offshore Louisiana (non-algae)
0.001661	0.007557	693.771	220.422	Offshore Louisiana (non-algae)
0.002043	0.006102	560.136	193.368	Offshore Louisiana (non-algae)
0.001962	0.004577	840.118	250.942	Offshore Louisiana (non-algae)
0.0013	0.007532	869.122	264.404	Offshore Louisiana (non-algae)
0.001696	0.007461	923.954	286.028	Offshore Louisiana (non-algae)
0.00224	0.009621	616.03	207.387	Offshore Louisiana (non-algae)
0.001302	0.005459	907.613	273.204	Offshore Louisiana (non-algae)
0.003788	0.001894	129.403	62.0874	Offshore Louisiana (non-algae)
0.000007	0.00427	859.853	279.547	Offshore Louisiana (non-algae)
0.001763	0.00274	116.734	59.86	Offshore Louisiana (non-algae)
0.001899	0.00129	119.528	59.5533	Offshore Louisiana (non-algae)
0.001644	0.000324	124.937	62.4096	Offshore Louisiana (non-algae)
0.006323	0.007149	460.591	220.441	Offshore Louisiana (algae)
0.001912	0.005573	154.153	106.843	Offshore Louisiana (algae)
0.000618	0.003823	151.25	110.134	Offshore Louisiana (algae)
0.000945	0.002293	145.641	105.258	Offshore Louisiana (algae)
0.000548	0.004845	387.074	190.34	Offshore Louisiana (algae)
0.000808	0.006808	353.808	181.809	Offshore Louisiana (algae)
0.000287	0.005317	356.126	183.496	Offshore Louisiana (algae)
0.001436	0.005368	657.971	282.285	Offshore Louisiana (algae)
0.003503	0.004789	676.34	286.455	Offshore Louisiana (algae)
0.003515	0.004289	570.689	250.257	Offshore Louisiana (algae)
0.000273	0.008353	707.298	300.213	Offshore Louisiana (algae)
-0.00041	0.004138	599.713	261.869	Offshore Louisiana (algae)
-0.00045	0.004479	541.073	242.318	Offshore Louisiana (algae)
0.000337	0.004531	582.379	255.151	Offshore Louisiana (algae)
0.000266	0.003058	563.766	252.12	Offshore Louisiana (algae)

0.000126	0.007843	488.643	222.025	Offshore Louisiana (algae)
0.001512	0.003872	256.461	115.64	Barataria Bay
0.00121	0.002404	207.214	96.6987	Barataria Bay
0.001825	0.006156	174.612	82.7265	Barataria Bay
0.001125	0.004228	104.259	57.2829	Barataria Bay
0.000451	0.005352	652.196	246.166	Barataria Bay
0.000027	0.005962	650.899	245.732	Barataria Bay
0.001393	0.004047	131.619	54.4398	Barataria Bay
0.000874	0.007406	928.116	328.571	Barataria Bay
0.000924	0.006493	906.132	321.209	Barataria Bay
0.00181	0.006986	905.412	321.557	Barataria Bay
0	0.004	83.41	65.07	Brackish LA coastal Bay A
0	0.0032	102.43	88.25	Brackish LA coastal Bay A
0	0.0019	26.51	19.81	Brackish LA coastal Bay A
0	0.0026	28.42	21.55	Brackish LA coastal Bay A
0.0016	0.0022	15.07	34.65	Brackish LA coastal Bay A
0.0017	0.0027	16.29	32.09	Brackish LA coastal Bay A
0.0012	0	16.42	29.93	Brackish LA coastal Bay A
0.0012	0.0028	13.11	24.76	Brackish LA coastal Bay A
0.0012	0.003	14.03	36.57	Brackish LA coastal Bay A
0.0009	0	12.17	19	Brackish LA coastal Bay A
0	0	12.65	9.98	Brackish LA coastal Bay A
0	0.0017	52.49	46.33	Brackish LA coastal Bay A
0	0	57	44.45	Brackish LA coastal Bay A
0	0	28.34	23.75	Brackish LA coastal Bay A
0	0	29.96	28.27	Brackish LA coastal Bay A
0.0007	0.0008	47.44	46.7	Brackish LA coastal Bay A
0	0	8.09	8.37	Brackish LA coastal Bay A
0	0	9.78	11.19	Brackish LA coastal Bay A
0	0.0046	42.89	35.21	Brackish LA coastal Bay A
0.0007	0.0032	47.04	35.2	Brackish LA coastal Bay A
0	0	24.75	19.06	Brackish LA coastal Bay A
0.0006	0	29.74	21.34	Brackish LA coastal Bay A
0	0.0038	25.72	31.72	Brackish LA coastal Bay A
0	0.003	29.7	37.78	Brackish LA coastal Bay A
0	0	36.9	32.49	Brackish LA coastal Bay A
0	0.0014	41.02	30.09	Brackish LA coastal Bay A
0.0007	0.0028	31.08	31.89	Brackish LA coastal Bay A
0	0.0032	48.9	46.47	Brackish LA coastal Bay A
0	0.0031	14.58	15.09	Brackish LA coastal Bay A
0.0007	0.0023	23.23	23.38	Brackish LA coastal Bay A
0	0	29.63	28.1	Brackish LA coastal Bay A
0	0.0033	43.4	38.25	Brackish LA coastal Bay A
0.0009	0.002	48.005	56.61	Brackish LA coastal Bay J
0.0002	0.0015	55.249	58.7	Brackish LA coastal Bay J
0.0005	0.0029	45.448	56.47	Brackish LA coastal Bay J
0	0.0029	39.571	46.38	Brackish LA coastal Bay J
0.001	0.0024	3.13	4.44	Brackish LA coastal Bay J
0.0003	0.0014	9.146	12.14	Brackish LA coastal Bay J
0.0005	0.004	67.162	71.54	Brackish LA coastal Bay J
0.0006	0.0037	100.85	126.29	Brackish LA coastal Bay J
0.0007	0.0012	29.664	28.66	Brackish LA coastal Bay J
0.0007	0.0023	30.849	26.96	Brackish LA coastal Bay J
0	0.0029	35.108	40.79	Brackish LA coastal Bay J
0	0.0036	42.861	43.51	Brackish LA coastal Bay J
0	0.002	40.376	36.65	Brackish LA coastal Bay J
0	0.0036	38.034	33.95	Brackish LA coastal Bay J
0	0.0029	24.162	34.65	Brackish LA coastal Bay J
0	0.0027	22.073	27.6	Brackish LA coastal Bay J
0	0.0043	29.523	44.02	Brackish LA coastal Bay J
0	0.0044	30.423	48.93	Brackish LA coastal Bay J

0.0011	0.0039	36.137	41.9	Brackish LA coastal Bay J
0	0.0028	38.049	44.6	Brackish LA coastal Bay J
0.0004	0.0029	60.041	65.91	Brackish LA coastal Bay J
0	0.0038	81.939	80.85	Brackish LA coastal Bay J
0.0008	0.0031	29.698	31.22	Brackish LA coastal Bay J
0	0.004	42.213	42.51	Brackish LA coastal Bay J
0	0.0037	37.387	44.58	Brackish LA coastal Bay J
0	0	45.305	53.49	Brackish LA coastal Bay J
0.001882192	0.006797816	281.9853872	91.22458282	Standard Deviation
0.001378678	0.004489661	248.1714174	105.1537562	Mean
0.0007	0.0038	100.85	62.0874	Median

***note: 0 = a concentration below ICP detection limits**

THE VITA

Sean Patrick Kenny grew up in southern Louisiana in the small town of Destrehan with his mother. He attended Destrehan High School and graduated in May 2005. He then attended college at Louisiana State University A&M in Baton Rouge, Louisiana, where he earned a Bachelor of Science degree in Biological Sciences with Chemistry minor in May 2010. He stayed in Baton Rouge to continue his education by beginning his Master of Science program at Louisiana State University A&M within the Department of Oceanography and Coastal Sciences in the Spring of 2011. He anticipates graduation in December 2013.